

Technology Assessment Report for Industrial
Boiler Applications. Oil Cleaning

Catalytic, Inc.
Charlotte, NC

Prepared for

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November 1979

Technology Assessment Report for Industrial Boiler Applications: Oil Cleaning

by

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**Contract No. 68-02-2604
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Washington, DC 20460**

FOREWORD

In the ensuing discussion of emission control technologies, candidate technologies were compared using three emission control levels labelled "moderate, intermediate, and stringent." These control levels were chosen only to encompass all candidate technologies and form bases for comparison of technologies for control of specific pollutants considering performance, costs, energy, and non-air environmental effects.

From these comparisons, candidate "best" technologies for control of individual pollutants are recommended by the contractor for consideration in subsequent industrial boiler studies. These "best technology" recommendations do not consider combinations of technologies to remove more than one pollutant and have not undergone the detailed environmental, cost, and energy impact assessments necessary for regulatory action. Therefore, the levels of "moderate, intermediate, and stringent" and the recommendation of "best technology" for individual pollutants are not to be construed as indicative of the regulations that will be developed for industrial boilers. EPA will perform rigorous examination of several comprehensive regulatory options before any decisions are made regarding the standards for emissions from industrial boilers.

PREFACE

The 1977 Amendments to the Clean Air Act required that emission standards be developed for fossil-fuel-fired steam generators. Accordingly, the U.S. Environmental Protection Agency (EPA) recently promulgated revisions to the 1971 new source performance standard (NSPS) for electric utility steam generating units. Further, EPA has undertaken a study of industrial boilers with the intent of proposing a NSPS for this category of sources. The study is being directed by EPA's Office of Air Quality Planning and Standards, and technical support is being provided by EPA's Office of Research and Development. As part of this support, the Industrial Environmental Research Laboratory at Research Triangle Park, N.C., prepared a series of technology assessment reports to aid in determining the technological basis for the NSPS for industrial boilers. This report is part of that series. The complete report series is listed below:

<u>Title</u>	<u>Report No.</u>
The Population and Characteristics of Industrial/ Commercial Boilers	EPA-600/7-79-178a
Technology Assessment Report for Industrial Boiler Applications: Oil Cleaning	EPA-600/7-79-178b
Technology Assessment Report for Industrial Boiler Applications: Coal Cleaning and Low Sulfur Coal	EPA-600/7-79-178c
Technology Assessment Report for Industrial Boiler Applications: Synthetic Fuels	EPA-600/7-79-178d
Technology Assessment Report for Industrial Boiler Applications: Fluidized-Bed Combustion	EPA-600/7-79-178e
Technology Assessment Report for Industrial Boiler Applications: NO _x Combustion Modification	EPA-600/7-79-178f
Technology Assessment Report for Industrial Boiler Applications: NO _x Flue Gas Treatment	EPA-600/7-79-178g
Technology Assessment Report for Industrial Boiler Applications: Particulate Collection	EPA-600/7-79-178h
Technology Assessment Report for Industrial Boiler Applications: Flue Gas Desulfurization	EPA-600/7-79-178i

These reports will be integrated along with other information in the document, "Industrial Boilers - Background Information for Proposed Standards," which will be issued by the Office of Air Quality Planning and Standards.

ABSTRACT

This study assesses the applicability of oil cleaning technology to industrial boilers and is one of a series of technology assessment reports to aid in determining the technological basis for a New Source Performance Standard for Industrial Boilers. The status of development and performance of alternative oil cleaning techniques were assessed and the cost, energy, and environmental impacts of the most promising processes were identified.

Hydrotreating processes (HDS) which produce cleaned liquid fuels are considered the best system of emission reduction applicable to oil-fired industrial boilers. The processes which clean oil by gasification are either not generally suited to the small scale of industrial boilers (POX) or are not commercially demonstrated (CAFB). The average capital investment, as well as the overall energy requirements, increase with increasing degree of desulfurization.

Sulfur oxide emissions and particulate emissions are highly dependent on the sulfur and ash contents of the oil, respectively. Nitrogen oxide emissions are dependent on fuel nitrogen content, as well as excess O_2 level and boiler size. In general, NO_x emissions decrease with decreasing excess O_2 and with increasing boiler size. The naturally low-sulfur, low-ash oils tended to meet at least the recommended control levels for moderate control in the oil cleaning category and quite often met even the intermediate or stringent control levels. The high-sulfur, high-ash oils, however, often failed to meet even moderate control levels, which suggests the need for oil cleaning. The use of HDS as an SO_2 control technology on industrial boilers results in the expenditure of 2-4% of the energy generated by the boilers. When the energy consumption of the hydrogen plant is factored into a total desulfurization energy consumed, the percentage of energy used increases substantially to 4.5 to 10.8%.

The cost impact of providing low sulfur distillate oil for firing small commercial boilers is minimal, amounting to just a 6.7% premium for 0.3% S and 7.7% premium for 0.1% S oil.

The cost impact of using residual fuel oil is much more dramatic, ranging from a premium of 6.7 to 18.6% when using oil desulfurized to a level of 1.6% S up to a premium of 39 to 43.1% when using oil desulfurized to a level of 0.1% S.

The cost of HDS escalates quite rapidly with the degree of desulfurization in a given oil going from \$0.91/B for a level of 1.6% sulfur to a cost of \$5.28/B for desulfurizing to a level of 0.1% sulfur.

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SECTION 1

EXECUTIVE SUMMARY

1.1 INTRODUCTION

Purpose of Report

The purpose of this report is to assess the available oil cleaning technology for control of emissions from oil-fired industrial boilers. Uncontrolled industrial boilers using oil fuels emit significant amounts of particulates, SO_x , and NO_x to the atmosphere. A recent study by PEDCo⁽¹⁾ provided the data shown in Table 1-1. PEDCo estimated the consumption of residual and distillate fuels in the industrial section at $19,881 \times 10^3$ m³/yr ($125,067 \times 10^3$ bbl/yr) and 7281×10^3 m³/yr ($45,799 \times 10^3$ bbl/yr), respectively, in 1975. In 1977, residual oil fuel supplied 27.3% of the Btu capacity of industrial/commercial boilers with distillate fuels providing 9.7%. Furthermore, PEDCo projects that oil-fired industrial/commercial boiler capacity will increase by approximately 2.3 times 1977 values by the year 2000. Obviously, without controls, emissions would increase roughly in proportion to fuel use.

Pollutant Formation Mechanisms

Sulfur oxide emissions are directly related to the sulfur content of the fuel. The combustion of cleaner, low-sulfur oil will result in lower SO_x emissions to the atmosphere. Nitrogen oxides are formed from both oil-bound nitrogen and nitrogen in the combustion air. Decreased nitrogen in fuels will reduce NO_x emissions, but it will not affect thermal fixation of atmospheric nitrogen. Staged combustion, low excess oxygen, and flue gas recirculation may be used for controlling NO_x emissions originating from thermal fixation of atmospheric nitrogen during the combustion of clean oils.⁽²⁾ Particulate emissions are dependent on the fuel characteristics, such as carbon residue and ash, which are reduced in oil treatment. Therefore, particulate loadings in general should be lower when cleaner fuels are being burned.

TABLE 1-1. ESTIMATED UNCONTROLLED EMISSIONS FROM THE
INDUSTRIAL/COMMERCIAL BOILER POPULATION⁽¹⁾

<u>Boiler Type</u>	<u>Estimated Emissions (1975) Mg/yr (tons/yr)</u>		
	<u>Particulate</u>	<u>SO_x</u>	<u>NO_x</u>
Water Tube			
Residual Oil Fired	59,900 (66,000)	794,500 (875,800)	198,600 (218,900)
Distillate Oil Fired	2,300 (2,500)	38,700 (42,700)	25,200 (27,800)
Fire Tube			
Residual Oil Fired	22,200 (24,500)	294,700 (324,900)	73,700 (81,200)
Distillate Oil Fired	3,200 (3,500)	53,700 (59,200)	34,900 (38,500)
Cast Iron			
Residual Oil Fired	14,500 (16,000)	192,200 (211,900)	48,000 (53,000)
Distillate Oil Fired	1,900 (2,100)	32,500 (35,800)	21,100 (23,300)
TOTALS - Residual Oil Fired	96,600 (106,500)	1,281,400 (1,412,600)	320,300 (353,100)
Distillate Oil Fired	7,400 (8,100)	124,900 (137,700)	81,200 (89,600)

Identification of Prime Control Mechanisms

There are two general approaches to reducing the emissions of SO_x , NO_x , and particulates from the burning of oil as a fuel in industrial boilers.

These are:

- 1) by cleaning the flue gas output from the boiler; and
- 2) by reducing the input of these impurities to the boiler
by precleaning the fuel

The first approach, called Flue Gas Cleaning, is being addressed by other contractors. This report discusses the oil cleaning techniques applicable to fuel oil fractions which are used as industrial boiler fuels.*

There are various methods of cleaning fuel oils which are used by refineries. The techniques fall into two general categories:

- 1) processes which produce a liquid fuel with reduced
contaminant content; and
- 2) processes which produce a gaseous fuel with reduced
contaminant content

The processes which produce cleaned liquid fuels are called hydrotreating. They are chemical processes involving contact of the oil with catalyst and hydrogen. These processes convert much of the chemically-bonded sulfur and nitrogen to gaseous hydrogen sulfide and ammonia, respectively, thereby removing them from the oil stream. In addition, the metals content of the oil is reduced, as is the carbon residue portion of the oil.

A second prime technique included in this report is the group of processes which is designed to convert heavy, high-sulfur residual oils to clean, low-sulfur gas. These processes include Partial Oxidation (POX) and the Chemically Active Fluid Bed Process (CAFB). The processes which produce liquid fuels are discussed under 1.2, and those which produce gaseous fuels are discussed under 1.3.

* A glossary of terms used in petroleum technology will be found in Appendix A.

1.2 HYDROTREATING PROCESSES FOR PRODUCING CLEANED LIQUID FUELS

In the typical hydrotreating process, atmospheric resid is filtered to remove rust, coke, and other suspended material. It is then mixed with hydrogen, heated to 650° to 850°F, and passed over one or more catalytic reaction beds.* Numerous chemical reactions occur which lead to removal of most of the sulfur as H_2S . Since sulfur is the major impurity in petroleum, the general technique is frequently called Hydrodesulfurization (HDS) in the industry.** However, the hydrogen reacts with other species besides sulfur compounds. For example, nitrogen compounds break down to liberate ammonia from the oil. This is called denitrogenation or denitrification. The nickel and vanadium in the oil, which are bound as organo-metal compounds, are liberated by reaction with the hydrogen. This is called demetallization. Most of the liberated metals deposit (as the sulfide) on the catalyst surface or in its pores and slowly deactivate the catalyst. Other reactions which take place break up large complex molecules such as asphaltenes and lead to a reduction in carbon residue of the product oil.

By utilizing catalysts, the reactions with hydrogen can be restricted largely to the types above which take place under moderate reaction conditions. Without the catalysts, higher reaction temperatures or pressures would be required; and, this would lead to greatly-increased hydrogen consumption due to hydrogenation of aromatic ring systems which are abundant in high-boiling petroleum fractions.

* The most widely-used catalysts are composites comprised of cobalt oxide, molybdenum oxide, and alumina, where alumina is the support carrying the other agents as promoters. However, other catalyst materials are in use or under development. Much of the catalyst technology is proprietary, but the patent literature is extensive. Ranney (3) has compiled information from over 200 patents during the period 1970-1975.

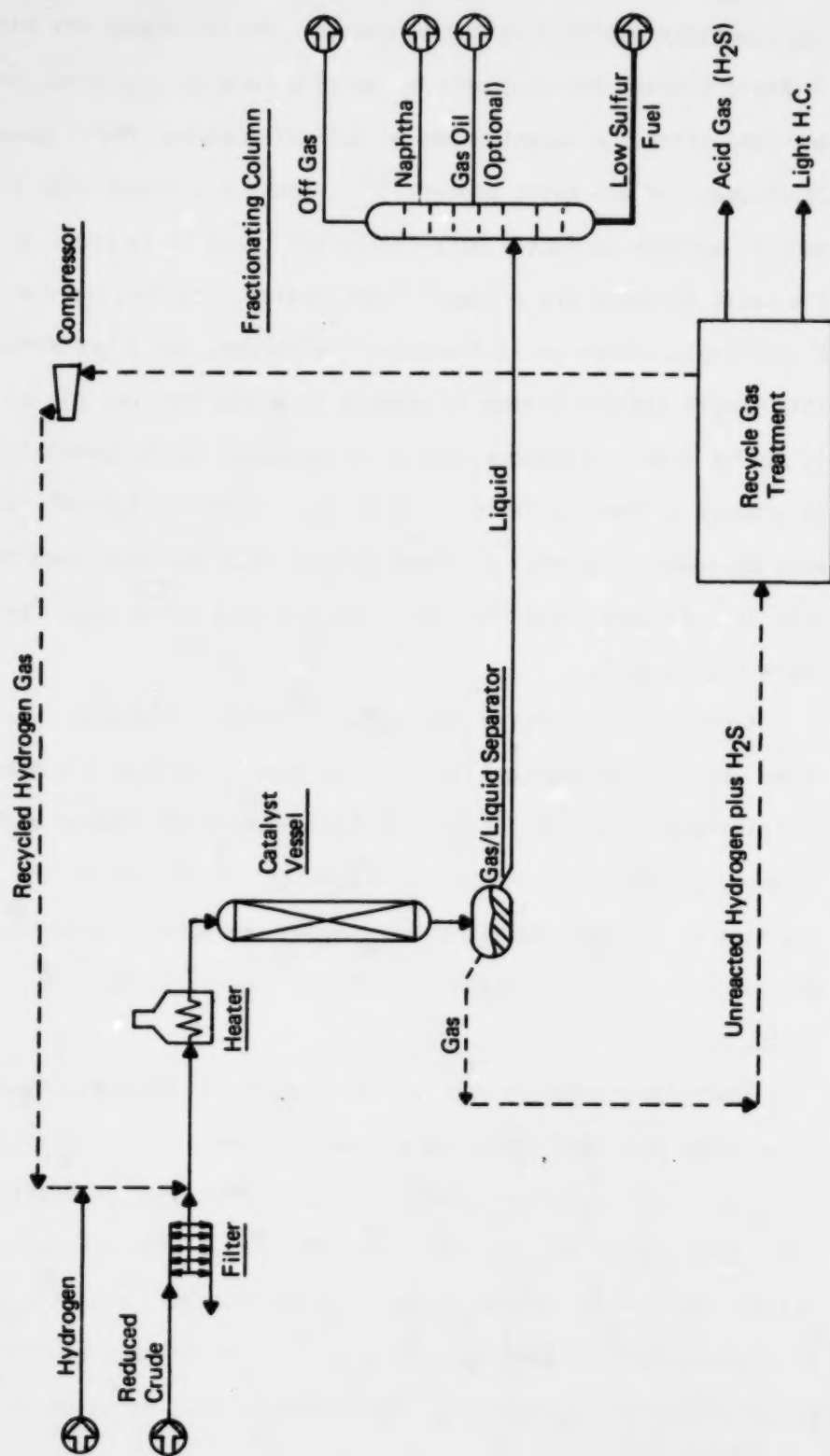
** A discussion of collection and processing techniques for the evolved H_2S will be found in Appendix B.

Many companies are engaged in developing and using catalytic hydrotreating (or hydrodesulfurization) processes. All processes are similar in basic concept and vary only in details such as catalysts, process conditions, and complexity. A recent paper by Gulf Oil Company investigators traces the development of one basic process.⁽⁴⁾ Figure 1-1 illustrates the simplest commercial version currently marketed by Gulf, and it is known as Gulf II HDS. Its basic elements are a feed filter, heater, single-stage catalytic reactor, a gas/liquid separator, a fractionating column, and a gas treatment section. This simple process system is capable of producing fuel oil of approximately 1% sulfur from a feedstock such as atmospheric resid containing 2-4% sulfur. To produce a lower sulfur content product, additional catalytic reaction stages must be added. The most advanced process Gulf has developed is known as Gulf IV. It uses three catalytic reactors and can produce fuel oils of approximately 0.1% sulfur.

Table 1-2 illustrates the typical product properties obtained when the three versions of the Gulf process are applied to Kuwait atmospheric resid containing 3.8% sulfur.⁽⁵⁾ It can be seen that the number of catalyst stages strongly affects both physical and chemical properties of the product oil. In addition to sulfur removal, other changes are noted: reduction in pour point and viscosity; and reduction of chemical impurities such as nitrogen, metals, salts, and ash.

There is a price to pay for such beneficial changes, however. The amount of hydrogen consumed increases with the degree of desulfurization. So does catalyst cost. A further cost is a slight reduction in heating value per gallon. Even though heating value/pound increases with the degree of desulfurization, the density of the product decreases; thus, slightly greater volumes of cleaned fuel oil must be burned to produce the same amount of heat provided by an untreated residual oil. The change in heating value is of the order of

Figure 1-1
BASIC HDS PROCESS (GULF HDS - TYPE II) (4)



Used with permission taken from: Frayer, J.A., et al., "Gulf's HDS Processes for High Metal Stocks," presented at the Japan Petroleum Institute, Tokyo, Japan, 8 May 1975.

TABLE 1-2. TYPICAL PROPERTIES OF LSFO PRODUCT FROM GULF HDS PROCESSES⁽⁵⁾

	<u>Untreated</u>	<u>Gulf II</u>	<u>Gulf III</u>	<u>Gulf IV</u>
Product Yield: Vol. %	--	89.4	97.5	97.1
Product Properties:				
Cut Point: °F	650	650	375	375
Gravity: °API	16.6	20.0	23.4	24.1
Sulfur: Wt. %	3.8	1.0	0.3	0.1
Carbon Residue: Wt. %	9.0	5.31	3.33	2.75
Nitrogen: Wt. %	0.22	0.13	0.13	0.09
Nickel: PPM	15.0	4.6	1.3	0.4
Vanadium: PPM	45.0	8.2	2.2	1.0
Viscosity: SLV (210°F)	250	107.3	52	45
Ash: Wt. %	0.02	0.004	0.003	0.003
Salt: PPM*	44.9	0	0	0
Heat of Combustion: Btu/LB	**	19,110	19,250	19,375
Hydrogen: Wt. %	**	12.1	12.5	12.7
Carbon: Wt. %	**	36.7	87.1	87.1
Pour Point: °F	**	+60	+35	0
Hydrogen Consumption: SCF/BBL	--	497	663	812

* Salt refers to all water-soluble cations, determined as halide and reported as NaCl before desalting.

** Not stated.

1-3% on atmospheric resids and about 5% on vacuum resids. When the degree of cleanup is considered, this energy impact seems insignificant.

The composition of the feedstock to a hydrotreater strongly influences the amount of hydrogen and catalyst consumption in the process. Nelson⁽⁶⁾ has correlated hydrogen consumption with sulfur reduction for a variety of resid feeds. For example, to obtain 90% reduction in sulfur for an 18°API feedstock, about 650 scf of hydrogen are consumed per barrel of oil processed whereas a 4°API feed would require 1200 scf/barrel. In another of Nelson's correlations, he plotted hydrogen consumption data for typical low metals atmospheric resid (16°API) and vacuum resid (6°API) as a function of sulfur desired in the fuel oil product. Thus, in producing 0.3-1.0% sulfur fuel oils from atmospheric resid, 345-775 scf of hydrogen per barrel are required, while vacuum resid requires 870 to 1150 scf to accomplish the same task. The problem caused by metals is deposition onto the catalyst surface or in the pores. This leads to deactivation of the catalyst, which is only overcome by an increase in bed temperature and/or hydrogen recirculation rate in order to maintain acceptable processing rates. Any increase in required severity of process conditions leads to more hydrocracking with a subsequent increase in hydrogen consumption.

A further complication from the metals content of the feed is a shortening of catalyst life. Even though some deactivation can be tolerated, the resultant increase in hydrogen uptake means catalyst must be changed out sooner. The effect of metals was shown in another Nelson correlation.⁽⁷⁾ As an example, for 90% sulfur removal from a 25 ppm metals content feedstock, about 27 barrels of oil can be processed per pound of catalyst; to achieve the same sulfur performance with a 100 ppm metals content feedstock, only 4.5 barrels can be processed per pound of catalyst; a 300 ppm feedstock requires almost one pound of catalyst per barrel. Clearly, high metal feedstocks are a costly problem to

the refiner. Most refiners are using a separate stage of lower cost catalyst material prior to the special hydrodesulfurization catalysts. These separate stages may be packed with a material such as alumina or clay, which collect the metals and "guards" the subsequent high activity catalyst. For this reason, some refiners call this stage a "guard reactor" or "guard vessel." Exxon uses such a system in their RESIDfining process.⁽⁸⁾

From the above, it is obvious that catalyst life is quite variable. In a fixed-bed system, catalyst changes are usually once or twice per year, depending on product requirement and feedstock composition. For example, with the Gulf IV system, producing 0.1% LSFO from 3.8% S Kuwait Resid (97% HDS), a catalyst life of six months is the design base. Similarly, using Arabian Heavy with RESIDfining at 75% HDS, a catalyst life of 400-500 days can be achieved.

Most refiners use fixed catalyst beds, which require a process shutdown for catalyst replacement. However, there are some advocates of expanded or ebullated beds with intermittent catalyst feed and bleed systems to maintain continuous operation at relatively constant conditions. The H-Oil process developed by Hydrocarbon Research, Inc. and utilized by Cities Service is an example of such an operating system. The expanded bed operates as a back mix reactor with the entire bed at a constant temperature. Such a system is less prone to plugging but has a slightly greater hydrogen consumption than a fixed bed system, according to Nelson.⁽⁶⁾ It is most suitable for high metals feedstocks where catalyst life is short.⁽⁷⁾

1.3 GASIFICATION PROCESSES FOR PRODUCING CLEAN GASEOUS FUELS

Process Description

Gasification processes can convert high-sulfur feedstocks into a fuel gas by controlled partial oxidation (POX) with air or oxygen. No catalyst is required; thus, a wide range of fuels can be converted to clean gaseous fuels. The desalted feedstock is partially oxidized at high temperature to form a

gaseous mixture of carbon monoxide (CO) and hydrogen (H_2) with a small amount of methane (CH_4). Carbon soot produced as a result of incomplete combustion is recycled back to the process. Either oxygen or air may be used for the partial oxidation, depending on the desired heating value of the product gas. When air is used, the nitrogen remains in the product gas. When oxygen is used, the peak temperatures are usually controlled by introducing a diluent such as steam or carbon dioxide.

In a typical application of this process,⁽⁹⁾ a heavy residuum and the oxidant (air or oxygen) are preheated with steam and fed to the reactor. The hot reactor effluent [2400°F (1316°C)] gas containing some ash from the feed and soot (1-3% by wt. of fuel) is passed to a specially-designed waste heat boiler which produces high pressure steam. The crude gas exiting the waste heat system [about 325°F (163°C)] is then passed into a carbon removal system, which consists of two units. The bulk of the carbon is removed by a special carbon-water contactor of proprietary design; the remaining carbon is removed by a cooler/scrubber water wash. The product gas contains less than 5 ppm carbon and virtually no ash or other particulates. It is directly usable for gas-turbine fuel after sulfur removal (see Appendix B for a discussion of processes for removal of H_2S from hydrocarbon gases).

The desulfurized product gas has a heating value of approximately 300 Btu/Scf when oxygen is used for the oxidation. By comparison, the product from air oxidation has a heating value of approximately 120 Btu/Scf because of the nitrogen remaining in the gas. Typical product-gas compositions for oxygen and air gasification are shown in Table 1-3.⁽⁹⁾

A recent development partially funded by the EPA has resulted in the design, construction, and testing of the Chemically Active Fluid Bed (CAFB) process demonstration unit in San Benito, Texas.⁽¹⁰⁾ The CAFB process is designed to produce a clean, low-sulfur gas by partially oxidizing a heavy,

TABLE 1-3. TYPICAL PRODUCT GAS COMPOSITION FROM GASIFICATION PROCESSES⁽⁹⁾

	<u>% vol., dry basis</u>	
	<u>O₂ Oxidation</u>	<u>Air Oxidation</u>
Hydrogen	48.0	12.0
Carbon Monoxide	51.0	21.0
Methane	0.6	0.6
Nitrogen	0.2	66.0
Argon	0.2	0.4
Sulfur*	<u>5 ppm</u>	<u>5 ppm</u>
Total	100.0	100.0

* after desulfurizing using Shell Sulfinol or ADIP process

Used with permission taken from: Kuhre, C. J. and J. A. Sykes, Jr.,
Energy Technology Handbook, D. M. Considine, Ed., McGraw-Hill Book Company,
 1977, pages 2-173 and 2-174.

high-sulfur feed in a limestone fluid bed. Hydrogen sulfide and some organic sulfur are absorbed by the lime. The remaining hot, low-sulfur fuel gas produced is ready for combustion. The CAFB reactor contains two sections; one for gasification of the feed, and one for regenerating the sulfur-containing limestone. During regeneration, air reacts with the spent stone, freeing the sulfur as sulfur dioxide. The sulfur dioxide is removed from the regeneration gas and may be recovered in a variety of processes. The limestone is then recycled to the gasification section until it loses its efficiency as an absorbent. This unit is currently scheduled for operation in the summer of 1979.

Commercial performance and reliability of the CAFB process are yet to be determined. Until this reliability is demonstrated, the CAFB concept is not likely to make a significant impact on the boiler-fuel picture. However, the simplicity and wide fuel flexibility of the CAFB as a front-end add-on make it a potentially very attractive new technology which could rapidly become important, especially for large new chemical complexes with several industrial boilers.

1.4 SELECTION OF THE BEST SYSTEM

The factors considered in the selection of the best system of emission reduction from those systems discussed above were:

1. Performance
2. Applicability
3. Status of Development
4. Cost Considerations
5. Energy Considerations
6. Environmental Considerations

In the selection process, an effort was made to rate each of the control systems against each of the selection criteria listed above. For each criterion, the best system was designated 1, the next best 2, etc. The lowest

overall score for all criteria was adjudged to be the best system. A summary of the rating evaluation is given in Table 1-4.

From these rating results, it is concluded that Hydrotreating (HDS) offers the best system of emission reduction for clean oil technology. A discussion of the ratings for the different selection criteria is given below:

- a) Performance - All three systems will yield a fuel that is environmentally acceptable for burning in a boiler. The overriding consideration in selecting HDS as the best system is its negligible or minor impact on boiler performance. Cleaned liquid fuels are directly applicable to existing industrial boilers with little negative impact on boiler performance. The modest reduction (1-3%) of heat content per gallon of cleaned oil will require additional fuel consumption to achieve rated boiler output. However, burning cleaner fuels will lower the severity of operation and maintenance on the boiler.
- b) Applicability - The HDS system is a clear selection for applicability, since the clean oil produced from HDS can be directly utilized in existing boilers with little impact on the boiler physical facilities. The gasification processes require the addition of equipment with attendant cost and space impacts. The retrofitting of either gasification process to an existing industrial boiler could, in some cases, be extremely difficult, if not impossible.

TABLE 1-4. RATING MATRIX FOR SELECTION OF BEST SYSTEM OF
EMISSION REDUCTION FOR CLEAN OIL TECHNOLOGY

<u>Control System</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>Total</u>
HDS	1	1	1	1	1	1	6
POX	2	2	2	3	2	3	14
CAFB	3	3	3	2	3	2	16

NOTE: Selection Criteria

1. Performance
2. Applicability
3. Status of Development
4. Cost Considerations
5. Energy Considerations
6. Environmental Considerations

c) Status of Development - Hydrotreating processing has been in commercial existence for more than 20 years, and over 20 hydrotreating processes are actively in use.⁽¹¹⁾ The current United States refinery desulfurization capacity is more than 1.8 million barrels per day from 86 plants. However, only 19 plants have direct resid or heavy gas oil hydrodesulfurization facilities which provide a total desulfurization capacity of approximately 0.6 million barrels per day.⁽¹²⁾

Hydrotreating is an extremely versatile process which is used to desulfurize, denitrogenate, and demetallize fuel oils prior to combustion. It can be adapted to a wide variety of feedstocks ranging from low-sulfur crude oils to high-sulfur residual oils. Hydrotreating used in conjunction with blending can produce fuel oils with almost any characteristics desired. Because of its versatility and widespread use, hydrotreating has been selected as the best candidate under the status of development criterion.

Partial oxidation is a commercially-proven process with more than 200 installations worldwide.⁽¹³⁾ It, too, is a versatile process that has been used with feedstocks ranging from natural gas through naphtha, residual oil, and even coal. Its primary use has been to produce synthesis gas for the manufacture of methanol or ammonia; however, there is no technical reason that the synthesis gas cannot be used as a boiler or turbine fuel. The process can be designed to use either air or oxygen as the

oxidizing medium, and the product gas will have a heating value of 120 Btu/SCF or 300 Btu/SCF dependent upon whether air or oxygen is used.

The Chemically Active Fluid Bed (CAFB) process is an attractive new technology which could become a significant factor over the next few years in both the utility and industrial areas. It, too, is a versatile process which can be used with a wide selection of feedstocks. The commercial performance and reliability of the CAFB process are yet to be determined. Until this reliability is demonstrated, the CAFB concept is not likely to make a significant impact on the boiler-fuel picture. A CAFB demonstration unit has been constructed and is currently undergoing testing at the La Palma station of Central Power and Light Company at San Benito, Texas.⁽¹⁴⁾

- d) Cost Considerations - The cost of upgrading liquid fuels in a few large refinery complexes is less demanding than individual emission control techniques at each industrial boiler. In the first place is the matter of mere numbers, wherein we are comparing the cost of desulfurization facilities at less than 100 refineries against individual emission control systems at literally thousands of industrial boiler installations. In addition, the economics of scale would greatly favor the installation of large central hydrotreating units at refineries rather than smaller installations at individual boilers. For example, a 150×10^6 Btu/hr oil-fired boiler requires approximately 25 barrels/hr of oil or 600 barrels per day. A typical

50,000 BPD HDS unit could supply nearly 85 such boilers. Preliminary cost figures show that typical hydrotreating facilities can be installed for investments ranging from \$500 per barrel per stream day capacity for moderate levels of emission control up to \$1,600 per barrel per stream day capacity for the most stringent levels of control.⁽¹⁵⁾ The costs of producing such cleaned fuels range from \$0.91 to as much as \$5.84 per barrel. The cost of partial oxidation units ranges from \$3,000 to \$6,000 per barrel per stream day with operating costs ranging from \$1.50 to \$7.00 per barrel.⁽¹⁶⁾ Cost information on CAFB units is very sketchy, but preliminary figures indicate an investment cost of \$3,500-\$4,500 per barrel per stream day and an operating cost of about \$4.00 per barrel.⁽¹⁶⁾

- e) Energy Considerations - The selection of hydrotreating under this criterion closely parallels the reasoning used for the cost considerations in that the selection is largely determined by numbers and sizes of units. The energy impacts are reflected by the operating cost figures given in the previous paragraph, which indicate that hydrotreating has advantages over both partial oxidation and chemically active fluid bed processing.
- f) Environmental Considerations - There is little difference between the three control systems from an environmental viewpoint. From a practical viewpoint, it is more advantageous to burn cleaned liquid fuels in industrial boilers rather than to handle the environmental problems of untreated

fuel oil at each industrial site. The control of potentially-hazardous pollutants can be more effectively managed at the refinery, and the emissions from combustion at industrial boilers can then be more effectively controlled by monitoring the fuel quality.

1.5 REGULATORY OPTIONS

Three regulatory options, which represent moderate, intermediate, and stringent levels of control for SO_2 , NO_x , and particulate emissions, have been selected. The selected emission levels were derived from actual emission data from industrial boilers.

Table 1-5 gives the maximum sulfur, nitrogen, and carbon residue content of cleaned fuel oil to meet the recommended control levels. The suggested regulatory options are based upon commercially-available systems for the production of low-sulfur fuels from high-sulfur feedstocks. The selected levels of control are based upon the use of residual fuel oil and represent the degree of desulfurization that can be attained using typical refinery processes and technology.

For the moderate level of control, a suggested fuel content of 0.8% sulfur, 0.3% nitrogen, and 12% carbon residue represents a residual fuel oil that is readily achievable from a number of refinery practices. For the stringent level of control, a suggested fuel content of 0.1% sulfur, 0.2% nitrogen, and 3% carbon residue represents the highest technically achievable residual fuel oil that can be attained with current technology. No U. S. refinery is currently producing such material, since there is no demand at present. For the intermediate level of control, the suggested fuel content of 0.3% sulfur, 0.2% nitrogen, and 6% carbon residue represents a technology which can be met by a number of available refinery processes, although only about 120,000 BPD capacity is currently installed in the U. S. An additional 75,000 BPD is coming on stream in 1980.⁽¹⁷⁾

TABLE 1-5. SUGGESTED POLLUTANT CONTENT OF CLEANED FUEL OIL
TO MEET RECOMMENDED CONTROL LEVELS

Pollutant	Control Level					
	Stringent		Intermediate		Moderate	
	Emission #/10 ⁶ Btu	Max. Fuel Content	Emission #/10 ⁶ Btu	Max. Fuel Content	Emission #/10 ⁶ Btu	Max. Fuel Content
SO ₂	0.1	0.1% S	0.3	0.3% S	0.8	0.8% S
NO _x	0.2	0.15% N	0.22	0.2% N	0.3	0.3% N
Particulates	0.05	3.0% C.R.*	0.1	6.0% C.R.	0.25	12% C.R.

*NOTE: % C.R. = weight percent carbon residue in fuel oil

1.6 ECONOMIC IMPACT OF BEST EMISSION CONTROL SYSTEM

As in Section 1.4, we selected hydrodesulfurization (HDS) as the best system of emission reduction for clean oil technology and recommended guideline control levels of regulatory options to best achieve moderate (0.8%S), intermediate (0.3%S), and stringent (0.1%S) levels of control.

In this section, we determine the cost of hydrodesulfurization to produce cleaned fuel oils to meet the required control limits and assess the economic impact of burning desulfurized oils in industrial boilers. In our cost analyses, only direct desulfurization of residual fuel oil is considered. Indirect desulfurization, or the procedure of desulfurizing a light distillate and back blending with residua to produce the required product level, is not capable of achieving the intermediate and stringent levels of control and therefore is not considered in this study.

The cost of hydrodesulfurization of residual fuel oil is a function not only of the sulfur content but also of the crude source from whence the residual was derived and the metal content of the residual. Since there are literally hundreds of different crude oils and, consequently, a like number of residua, it is virtually impossible to select a typical residual oil that would be representative of all these crudes. Accordingly, we have selected a group of five residual oils which cover a range of sulfur and metal values and which will accommodate virtually all the known crudes within the limits covered by these five residua. The five residua considered in this section can be classified as follows:

<u>Residua</u>	<u>Classification</u>
1. Ceuta	Low Sulfur, high metals
2. E. Venezuelan	Low sulfur, high metals
3. Kuwait	Medium sulfur, low metals
4. Khafji	High sulfur, moderate metals
5. Cold Lake	High sulfur, high metals

The cost of hydrodesulfurization is also highly dependent upon the degree of desulfurization. In order to cover as wide a range as possible, the hydrodesulfurization costs were calculated for the three recommended levels of control, as well as the State Implementation Plan (S.I.P.) level of 1.6% sulfur currently being used in most of the United States.

A summary of the hydrodesulfurization costs for the five residual fuel oils and four levels of sulfur content is given in Table 1-6.

TABLE 1-6. SUMMARY COSTS OF HYDRODESULFURIZATION OF RESIDUAL FUEL OIL

<u>Residual Fuel Oil</u>		<u>Percent Sulfur in Treated Oil</u>				
<u>Type</u>	<u>% Sulfur</u>	<u>ppm (Ni + V)</u>	<u>1.6 \$/bbl</u>	<u>0.8 \$/bbl</u>	<u>0.3 \$/bbl</u>	<u>0.1 \$/bbl</u>
Ceuta	2.12	292	0.91	2.28	3.91	5.28
E. Venezuelan	2.38	274	1.17	2.45	3.93	5.71
Kuwait	3.80	60	1.80	2.49	3.14	3.51
Khafji	4.36	118	2.20	2.35	3.60	4.11
Cold Lake	4.55	236	2.52	3.42	4.53	5.84

As evidenced from the foregoing table, the cost of HDS ranges from a low of \$0.91 per barrel for the hydrodesulfurization of a low-sulfur, high-metals residua to a high of \$5.84 per barrel for the hydrodesulfurization of a high-sulfur, high-metals residua.

It is also evident that the cost of HDS escalates quite rapidly with the degree of desulfurization, going from \$0.91/bbl for the desulfurization of Ceuta residual to a level of 1.6% sulfur to a cost of \$5.28/bbl for desulfurizing to a level of 0.1% sulfur. This represents a cost of \$14.46/bbl for the 1.5% S Ceuta oil, or 39% over the cost of untreated oil.

The foregoing table also indicates that the cost of desulfurization to the S.I.P. (1.6% S) and moderate (0.8% S) levels is primarily a function of the sulfur level of the untreated oil; whereas, desulfurizing to the intermediate (0.3% S) and stringent (0.1% S) levels clearly reflects the influence of metals content on desulfurization cost. It further shows that, regardless of the type of residual feed, the cost of desulfurizing to very low levels such as 0.1% S is substantial, ranging from \$3.51 to \$5.84 per barrel or 26 to 43% more than the cost of untreated oil.

Table 1-7 gives a cost breakdown into the principal cost elements. This table vividly illustrates the effect of hydrogen and catalyst costs on the overall cost of desulfurization which ranges from 33 to 61% of the total cost.

Table 1-8 gives the cost impact of low sulfur fuel oil firing in industrial boilers. Data are presented for small (4.4MW, 15,000 MBtu/hr) commercial-type boilers and for large (44MW, 150,000 MBtu/hr) industrial-type boilers. From Table 1-8, it is evident that the cost impact of providing low-sulfur distillate oil for firing small commercial boilers is minimal, amounting to just a 6.7% premium for 0.3% S and 7.7% premium for 0.1% S oil. This small effect is primarily brought about as a result of the small amount of desulfurization required to desulfurize regular No. 2 distillate oil, which usually contains 0.5% (or less) sulfur, to these lower sulfur levels.

The cost impact of using residual fuel oil is much more dramatic, ranging from a premium of 6.7 to 18.6% when using oil desulfurized to a level of 1.6% S up to a premium of 39 to 43.1% when using oil desulfurized to a level of 0.1% S.

TABLE 1-7. COST DISTRIBUTION FOR THREE RESIDUA (¢/bbl)

<u>Residual Oil</u>	<u>Percent Sulfur in Treated Oil</u>			
	<u>1.6</u>	<u>0.8</u>	<u>0.3</u>	<u>0.1</u>
Ceuta				
Labor	6.9	6.9	6.9	6.9
Utilities	24.9	49.7	62.0	65.7
Investment, Maint., & Waste Disposal	31.5	70.1	105.8	129.6
Hydrogen	21.0	67.0	102.0	117.0
Catalyst	9.0	38.0	121.0	216.0
Total	93.3	231.7	397.7	535.2
Sulfur Credit	2.0	5.0	6.9	7.6
Net Cost	91.3	226.7	390.8	527.6
Kuwait				
Labor	6.9	6.9	6.9	6.9
Utilities	47.8	59.4	73.4	76.9
Invest., Maint., & Waste Disposal	64.4	91.1	119.6	141.8
Hydrogen	58.0	88.0	107.0	115.0
Catalyst	11.0	15.0	20.0	24.0
Total	188.1	260.4	326.9	364.6
Sulfur Credit	8.3	11.3	13.2	13.9
Net Cost	179.8	249.1	313.7	350.7
Cold Lake				
Labor	6.9	6.9	6.9	6.9
Utilities	54.2	64.8	80.4	82.9
Invest., Maint., & Waste Disposal	97.1	116.0	139.5	156.9
Hydrogen	70.0	96.0	113.0	120.0
Catalyst	35.0	72.0	129.0	234.0
Total	263.2	355.7	468.8	600.7
Sulfur Credit	11.1	14.1	16.0	16.7
Net Cost	252.1	341.6	452.8	584.0

TABLE 1-8. COST IMPACT OF LOW SULFUR FUEL OIL FIRING IN BOILERS

System Standard Boilers Heat Input MW (MBTU/HR)	Type	Type & Level of Control	Crude Source	Control Efficiency (%S)	Annual Costs		Cost Impact	
					\$/kJ/S	\$/MBTU/ HR	% Over Uncon- trolled	% Over S.I.P. Controlled
44 (150,000)	Watertube	LSFO	Ceuta	S.I.P. Moderate Intermediate Stringent	1.6	4.03	1.18	N/A
					0.8	10.03	2.94	9.47
					0.3	17.23	5.05	20.75
					0.1	23.27	6.82	30.22
					1.6	5.15	1.51	N/A
					0.8	10.78	3.16	8.70
	Firetube	LSFO	E. Venezuelan	S.I.P. Moderate Intermediate Stringent	0.3	17.30	5.07	18.75
					0.1	25.15	7.37	30.85
					1.6	7.92	2.32	N/A
					0.8	10.95	3.21	4.50
					0.3	13.82	4.05	8.73
					0.1	15.46	4.53	11.14
44 (15,000)	Firetube	LSFO	Kuwait	S.I.P. Moderate Intermediate Stringent	1.6	9.69	2.84	N/A
					0.8	12.56	3.68	4.12
					0.3	15.87	4.65	8.89
					0.1	18.12	5.31	12.12
					1.6	11.09	3.25	N/A
					0.8	15.08	4.42	5.60
	Firetube	Distillate Fuel Oil	Cold Lake	S.I.P. Moderate Intermediate Stringent	0.3	19.96	5.85	12.50
					0.1	25.73	7.54	20.66
					1.6	9.69	2.84	N/A
					0.8	12.56	3.68	4.12
					0.3	15.87	4.65	8.89
					0.1	18.12	5.31	12.12
4.4 (15,000)	Firetube	LSFO	N/A	S.I.P. Moderate Intermediate Stringent	1.6	11.09	3.25	N/A
					0.8	15.08	4.42	5.60
					0.3	19.96	5.85	12.50
					0.1	25.73	7.54	20.66
					1.6	9.69	2.84	N/A
					0.8	12.56	3.68	4.12
	Firetube	Distillate Fuel Oil	N/A	S.I.P. Moderate Intermediate Stringent	0.3	19.96	5.85	12.50
					0.1	25.73	7.54	20.66
					1.6	9.69	2.84	N/A
					0.8	12.56	3.68	4.12
					0.3	15.87	4.65	8.89
					0.1	18.12	5.31	12.12

Table 1-9 shows the cost effectiveness of fuel oil desulfurization for the five residua considered, as well as the distillate fuel oil. Generally, these data indicate that the cost effectiveness improves as the sulfur content of the residuum feed rises, provided that the metal content does not increase as well.

A comparison of the Kuwait and Khafji data shows the effect of similarity between sulfur levels combined with relatively similar metal levels. The Cold Lake data vividly show the strong effect of high-metal levels.

The data of Table 1-9 also indicate that, for a given feedstock, fuel oil desulfurization tends to be less cost effective as the degree of desulfurization increases. This effect ranges from 17% to 65%, depending on the specific residuum; but, the trend is quite general.

1.7 ENERGY IMPACT OF BEST SYSTEM

Based upon the rating factors developed in Section 1.4, hydrodesulfurization was selected as the best system for emission reduction for clean oil technology. The HDS process cannot be considered on a stand-alone basis for the energy impact assessment, since auxiliary processes are required to dispose of process by-products. These auxiliary processes include a hydrogen sulfide absorption unit (circulating amine type), sulfur recovery with tail-gas scrubbing (Claus type with reduction system and tail-gas reheat), and sour water stripper (steam stripping), and a hydrogen plant.

The production of low-sulfur distillate and residual fuel oils by pre-combustion treatment methods such as hydrodesulfurization has the advantage of scale from the energy impact point of view. The HDS unit is centralized, with the attendant benefits of a large-scale operation. However, HDS systems require significant energy to operate. The process itself consumes about 2-4% of the energy content of the oil produced. When the energy consumption of the hydrogen plant is factored in, the percentage of energy used increases

TABLE 1-9. COST EFFECTIVENESS

Crude Source	Sulfur In Fuel Oil %	Cost/Unit Removal	
		\$/lb	\$/KG
Ceuta	1.6	0.52	1.14
	0.8	0.51	1.13
	0.3	0.64	1.40
	0.1	0.78	1.71
E. Venezuelan	1.6	0.45	0.99
	0.8	0.46	1.01
	0.3	0.56	1.23
	0.1	0.74	1.63
Kuwait	1.6	0.24	0.53
	0.8	0.25	0.55
	0.3	0.27	0.59
	0.1	0.28	0.62
Khafji	1.6	0.24	0.53
	0.8	0.24	0.53
	0.3	0.26	0.57
	0.1	0.29	0.64
Cold Lake	1.6	0.25	0.55
	0.8	0.27	0.59
	0.3	0.32	0.70
	0.1	0.39	0.86
Distillate	0.2	0.20	0.44
	0.1	0.21	0.46

substantially. The data below indicate the total desulfurization energy expenditure as a percentage of total boiler energy generated for the various sulfur control levels:

<u>Sulfur in Fuel Oil</u>	<u>Energy Consumed As a Percentage of Energy Generated</u>
1.6% S	4.5%
0.8% S	5.6%
0.3% S	8.6%
0.1% S	10.8%

Table 1-10 shows energy consumption for the HDS and hydrogen plant utilities as a function of desulfurization levels. It is apparent that, to achieve the lower sulfur level fuels (0.3% S or 0.1% S) for industrial boiler combustion without controls, substantial energy inputs are needed as the degree of desulfurization increases.

1.8 ENVIRONMENTAL IMPACT

A basic fuel oil refinery without an HDS system produces a variety of waste products which include air and water pollutants, as well as solid waste products. As a baseline, the data shown in Table 1-11 indicate the amounts of such pollutants produced. (18)

As a consequence of adding an HDS unit, there are only minor increases in the quantities of air and water pollutants produced. The major waste product comes from spent catalyst. With regard to the air emissions, the important factor to be considered is the net impact, i.e., reduction of emissions in industrial boilers versus increased refinery emissions.

First to be considered are the emissions to the air. Table 1-12 shows emissions of SO_x , NO_x , and particulate for uncontrolled (3.0% S), 0.8% S, and 0.1% S for the refinery processes and for industrial boiler combustion. Over the range from 3.0% to 0.1%, the refinery emissions increase slightly for

TABLE 1-10. ENERGY CONSUMPTION FOR SULFUR LEVEL-OF-CONTROLS IN RESIDUAL OIL

Crude Class	Utility	Sulfur in Fuel Oil			
		1.6%	0.8%	0.3%	0.1%
Low Sulfur 3% S	Power	2.9	6.4	8.2	8.7
	Steam	12.8	28.3	44.4	48.6
	Fuel	107.7	262.9	360.0	398.7
	Cooling Water	.31	.63	1.1	1.2
Med. Sulfur 3-4% S	Power	5.8	7.7	10.0	10.5
	Steam	31.0	43.8	63.8	71.2
	Fuel	227.5	314.8	364.2	393.1
	Cooling Water	.65	.94	1.2	1.2
High Sulfur 4% S	Power	7.0	8.9	10.7	11.0
	Steam	37.4	49.2	79.6	84.4
	Fuel	257.4	334.0	382.2	403.1
	Cooling Water	.75	.99	1.15	1.23

NOTE: Utility Units
 Power in KWH/Bbl
 Steam in MBtu/Bbl
 Fuel in MBtu/Bbl
 Cooling Water in MGal/Bbl

TABLE 1-11. ENVIRONMENTAL IMPACT OF A FUEL OIL REFINERY
PRODUCING 3.0% S RESIDUAL AND 0.5% S DISTILLATE OILS⁽¹⁸⁾

Air Emissions		(lb./M BBL Crude Processed)
Particulates		63.2
SO _x		160.0
NO _x		118.3
CO		12.0
Hydrocarbons		740
Water		(lb./M BBL Crude Processed)
Suspended Solids		2.5
Dissolved Solids		92.6
Organic Material		0.5
Solid Wastes		(lb./M BBL Crude Processed)
Catalysts		20
Other*		60

Source: "Environmental Problem Definition for Petroleum Refineries, Synthetic Natural Gas Plants, and Liquefied Natural Gas Plants," Radian Corp., November 1975, EPA-600/2-75-068.

* Includes: (1) entrained solids in the crude; (2) corrosion products; (3) silt from drainage and influent water; (4) maintenance and cleaning solids; and (5) waste water treatment facilities.

TABLE 1-12. ESTIMATED AIR EMISSIONS SUMMARY

Emission Sources	SO _x (1b/10 ⁶ Btu Fuel Oil)			NO _x (1b/10 ⁶ Btu Fuel Oil)			Particulate (1b/10 ⁶ Btu Fuel Oil)		
	<u>3.0%S</u>	<u>0.8%S</u>	<u>0.1%S</u>	<u>3.0%S</u>	<u>0.8%S</u>	<u>0.1%S</u>	<u>3.0%S</u>	<u>0.8%S</u>	<u>0.1%S</u>
Refinery Processes	.023	.030	.05	.019	.019	.019	.010	.010	.010
Industrial Boiler Combustion	<u>3.170</u>	<u>0.85</u>	<u>0.11</u>	<u>0.40</u>	<u>0.30</u>	<u>0.11</u>	<u>0.22</u>	<u>0.12</u>	<u>0.05</u>
Total	3.193	0.88	0.25	0.419	0.32	0.22	0.23	0.13	0.06

SO_x and remain constant for NO_x and particulate. In marked contrast, all three pollutants drop sharply as a result of using cleaner fuels at the industrial boiler. In the sulfur case, while refinery emissions increased from $.02 \text{ \#/}10^6 \text{ Btu}$ to $0.05 \text{ \#/}10^6 \text{ Btu}$, the industrial boiler emission drops from $3.2 \text{ \#/}10^6 \text{ Btu}$ to $0.11 \text{ \#/}10^6 \text{ Btu}$. The other two pollutants drop significantly, but not as dramatically.

The water pollution picture is not nearly as significant. Table 1-13 shows the baseline wastewater effluents for a 200,000 Bbl/day refinery. Sulfur as H_2S is about 0.1 ppm, but 3×10^6 gallons are discharged daily, i.e., about $2.5 \text{ \# H}_2\text{S/day}$. Adding a 50,000 Bbl/day HDS unit would not increase the water emissions significantly, since so little water actually stays in contact with the sulfur compounds. Estimates from data in Section 6 indicate that less than a 1% increase in waterborne H_2S effluent would result from residual oil desulfurization to the stringent level. This seems anomalous, but nearly all the sulfur compounds are converted to elemental sulfur with highly efficient cleanup processes.

The solid waste situation is quite different. In the past, if HDS catalyst activity could no longer be restored by carbon burnoff, i.e., metal poison accumulation was the limiting factor, the catalyst was discarded in a suitable landfill. With the soaring cost of catalyst (due to large recent price increases for cobalt in particular), metal recovery is beginning to alter the disposal picture. In order to estimate worst case, i.e., all HDS catalyst disposed of as hazardous waste, the following conservative assumptions were made:

- 1) U. S. HDS capacity of 600,000 Bbl/day for residual and vacuum gas oil HDS
- 2) Four types of residual oil used (worse than being used)

TABLE 7-13. REFINERY WASTEWATER EFFLUENT QUALITY FOR
 3×10^6 GAL/DAY (200,000 BBL/DAY CRUDE FEED) (18)

	<u>Concentration</u>
BOD	15 ppm
COD	80 ppm
Ammonia	2 ppm
Hydrogen Sulfide	0.1 ppm
Total Phosphorus	2 ppm
Phenols	0.1 ppm
Oil and Grease	2 ppm
Suspended Solids	10 ppm
Dissolved Solids	370 ppm

Source: "Environmental Problem Definition for Petroleum Refineries,
 Synthetic Natural Gas Plants, and Liquified Natural Gas
 Plants," Radian Corporation, November 1975, EPA-600/2-75-068.

- 3) catalyst consumption rates for desulfurization to 0.8, 0.3, and 0.1% S

The data obtained from these calculations follows:

<u>Residual Oil</u>	<u>Spent Catalyst Generation for Sulfur Control Levels in Tons/yr</u>		
	<u>0.8% S LSF0</u>	<u>0.3% S LSF0</u>	<u>0.1% S LSF0</u>
1. Low Sulfur, High Metals	20,000	64,000	115,000
2. High Sulfur, High Metals	38,000	69,000	125,000
3. Low Sulfur, Low Metals	8,000	11,000	13,000
4. High Sulfur, Low Metals	17,000	29,000	38,000

As an indication that the worst case scenario is very conservative, the actual U. S. HDS catalyst market has been estimated at 10,000-12,000 tons/yr.⁽¹⁹⁾ This value is probably quite a bit more accurate than our calculated range, primarily because of our using only residual oil in the calculations when, in fact, much of the U. S. capacity is from vacuum gas oil which has a much lower metal content than resids. Thus, catalyst life is likely to be several times longer. Also, catalyst regeneration efficiencies of 90-95% can be achieved by carbon burnoff, since metal accumulation is very slow with gas oils.

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SECTION 2

OIL CLEANING AND CLEAN OIL EMISSION CONTROL TECHNIQUES FOR OIL-FIRED INDUSTRIAL BOILERS

2.1 PRINCIPLES OF CONTROL

Sources of Emissions

Uncontrolled industrial boilers using oil fuels emit significant amounts of particulates, SO_x , and NO_x to the atmosphere. A recent study by PEDCo⁽¹⁾ provided the data shown in Table 2-1. PEDCo estimated the consumption of residual and distillate fuels in the industrial section at $19,881 \times 10^3$ m³/yr ($125,067 \times 10^3$ bbl/yr) and 7281×10^3 m³/yr ($45,799 \times 10^3$ bbl/yr), respectively, in 1975.⁽²⁾ In 1977, residual oil fuel supplied 27.3% of the Btu capacity of industrial/commercial boilers with distillate fuels providing 9.7%. Furthermore, PEDCo projects oil-fired industrial/commercial boiler capacity to increase by approximately 2.3 times 1977 values by the year 2000.⁽³⁾ Obviously, without controls, emissions would increase roughly in proportion to fuel use.

Pollutant Formation Mechanisms

Sulfur oxide emissions are directly related to the sulfur content of the fuel. The combustion of cleaner, low-sulfur oil will result in lower SO_x emissions to the atmosphere. Nitrogen oxides are formed from both oil-bound nitrogen and nitrogen in the combustion air. Decreased nitrogen in fuels will reduce NO_x emissions, but it will not affect thermal fixation of atmospheric nitrogen. Staged combustion, low excess oxygen, and flue gas recirculation may be used for controlling NO_x emissions originating from thermal fixation of atmospheric nitrogen during the combustion of clean oils.⁽⁴⁾ Particulate emissions are dependent on the fuel characteristics, such as carbon residue and ash, which are reduced in oil treatment. Therefore, particulate loadings in general should be lower when cleaner fuels are being burned.

TABLE 2-1. ESTIMATED UNCONTROLLED EMISSIONS FROM THE
INDUSTRIAL/COMMERCIAL BOILER POPULATION (1)

Boiler Type	Estimated Emissions (1975) Mg/yr (tons/yr)		
	Particulate	SOx	NOx
Water Tube			
Residual Oil Fired	59,900 (66,000)	794,500 (875,800)	198,600 (218,900)
Distillate Oil Fired	2,300 (2,500)	38,700 (42,700)	25,200 (27,800)
Fire Tube			
Residual Oil Fired	22,200 (24,500)	294,700 (324,900)	73,700 (81,200)
Distillate Oil Fired	3,200 (3,500)	53,700 (59,200)	34,900 (38,500)
Cast Iron			
Residual Oil Fired	14,500 (16,000)	192,200 (211,900)	48,000 (53,000)
Distillate Oil Fired	1,900 (2,100)	32,500 (35,800)	21,100 (23,300)
TOTALS			
Residual Oil Fired	96,600 (106,500)	1,281,400 (1,412,600)	320,300 (353,100)
Distillate Oil Fired	7,400 (8,100)	124,900 (137,700)	81,200 (89,600)

Relative Emission Levels

As previously indicated, the SO_x , NO_x , and particulate emission levels from oil-fired boilers are highly dependent on the quality of fuel being burned. For example, SO_x emissions may range from 3.5 lb. SO_x per million Btu for a high-sulfur residual oil to 0.1 lb. SO_x per million Btu for a clean, desulfurized fuel oil. Similarly, NO_x emission levels may range from 0.6 lb. NO_x per million Btu to 0.3 lb. NO_x per million Btu for a denitrogenized fuel oil. Total particulate loadings may range from 0.1 lb. particulates per million Btu to 0.03 for a clean fuel.

Identification of Prime Control Mechanisms

There are two general approaches to reducing the emissions of SO_x , NO_x , and particulates from the burning of oil as a fuel in industrial boilers. These are:

- 1) by cleaning the flue gas output from the boiler; and
- 2) by reducing the input of these impurities to the boiler by precleaning the fuel.

The first approach, called Flue Gas Cleaning, is being addressed by other This report discusses the oil cleaning techniques applicable to fuel oil fractions which are used as industrial boiler fuels.

There are various methods of cleaning fuel oils which are used by refineries. The techniques fall into two general categories:

- 1) processes which process a liquid fuel with reduced contaminant content; and
- 2) processes which produce a gaseous fuel with reduced contaminant content.

A brief background on oil refining may be of benefit to readers who are not familiar with the petroleum field. A glossary of terms used in petroleum technology will be found in Appendix A.

Petroleum (or crude oil) is a very complex mixture of chemical compounds which are comprised mainly of carbon, hydrogen, sulfur, nitrogen, oxygen, and metals. Crude oils vary widely in composition and boiling range depending on their origin. They also frequently contain inorganic salts from brine found with the crude or from seawater used as ballast in tankers for shipment.

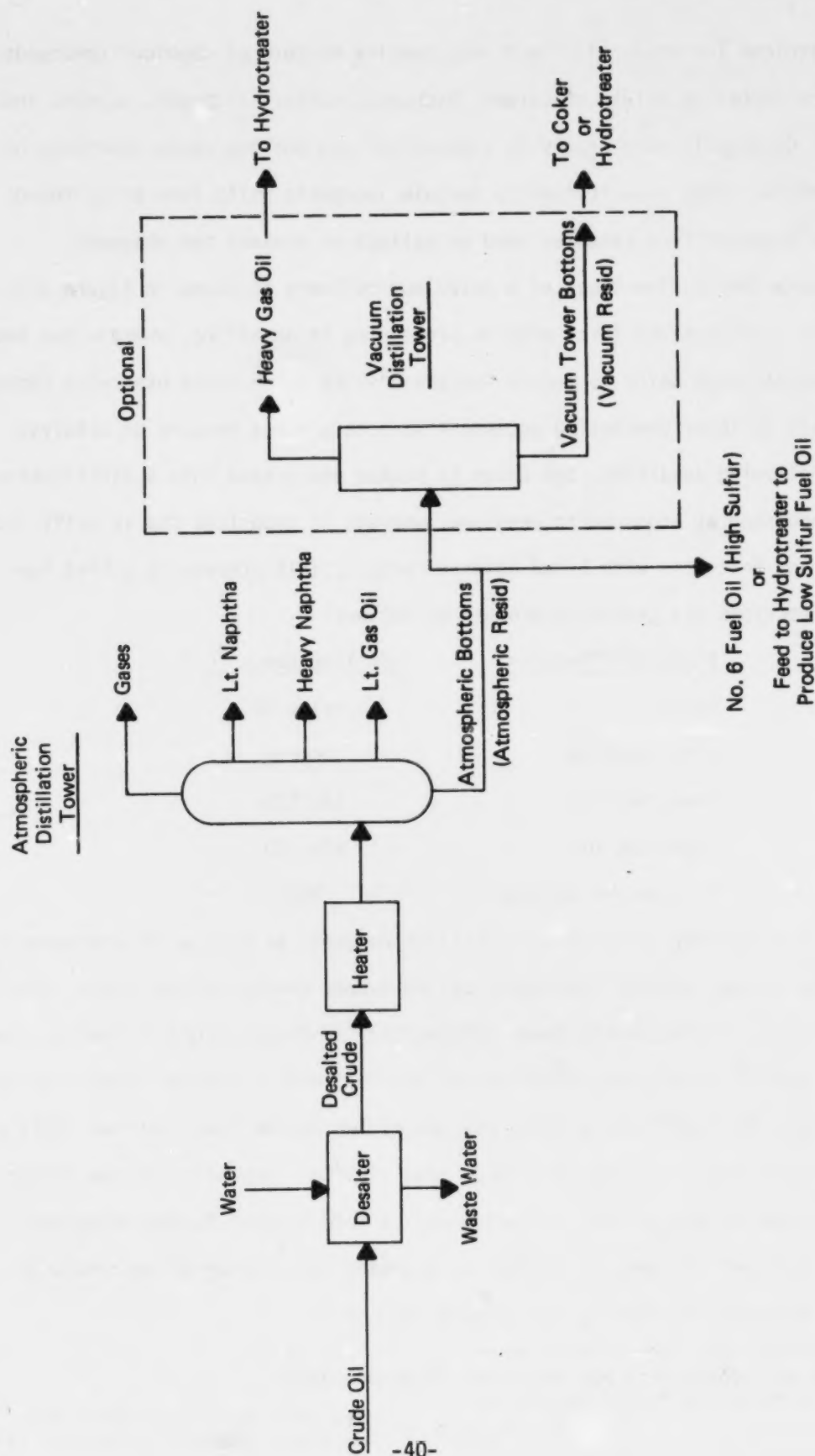
A very simple flow sheet of a petroleum refinery is given in Figure 2-1. It can be seen that the first step in processing is desalting, wherein the crude oil is washed with water to remove inorganic salts which would otherwise corrode or deposit in later processing equipment such as process heaters or catalyst beds. Following desalting, the crude is heated and passed into a distillation column operated at atmospheric pressure, wherein it vaporizes and is split into a number of fractions with broad boiling ranges. This process is called topping. Fractions are generally grouped as follows:

<u>Crude Oil Fraction</u>	<u>Boiling Range °F *</u>
Gases	below 80
Light Naphtha	80-220
Heavy Naphtha	180-520
Light Gas Oil	420-650
Atmospheric Bottoms	650+

If the refinery has a vacuum distillation unit, as well as an atmospheric unit, the bottoms product (variously called topped crude, reduced crude, atmospheric resid, or atmospheric tower bottoms) may be fractionated further to give a heavy gas oil (sometimes called vacuum gas oil) with a boiling range from approximately 700-1100°F and a heavy residue called Vacuum Tower Bottoms (VTB) or Vacuum Resid (VR) with a boiling range from 1050°F+. Depending on the refinery's design purposes, the various fractions may be sold without further treatment, blended for fuel oil use, or refined or upgraded into higher-priced products such as gasoline, lubricants, and cleaner fuel oils.

* Ranges are approximate and vary with crude processed and individual refinery systems. (5)

Figure 2-1
SIMPLIFIED CRUDE OIL REFINERY FLOWSHEET FOR FUEL OIL PRODUCTION



The processes which produce cleaned liquid fuels are called hydrotreating. They are chemical processes involving contact of the oil with catalyst and hydrogen. These processes convert much of the chemically-bonded sulfur and nitrogen to gaseous hydrogen sulfide and ammonia respectively, thereby removing them from the oil stream. In addition, the metals content of the oil is reduced, as is the carbon residue portion of the oil.

A second prime technique included in this report is the group of processes which is designed to convert heavy, high-sulfur residual oils to clean, low-sulfur gas. These processes include Partial Oxidation (POX) and the Chemically Active Fluid Bed Process (CAFB). The processes which produce liquid fuels are discussed under 2.2, and those which produce gaseous fuels are discussed under 2.4.

2.2 HYDROTREATING PROCESSES FOR PRODUCING CLEANED LIQUID FUELS

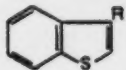
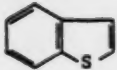
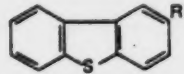
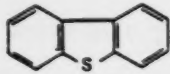
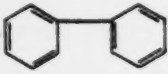
In the typical hydrotreating process, atmospheric resid is filtered to remove rust, coke, and other suspended material. It is then mixed with hydrogen, heated to 650⁰ to 850⁰F, and passed over one or more catalytic reaction beds.* Numerous chemical reactions occur which lead to removal of most of the sulfur as H₂S. Table 2-2 illustrates some of the types of compounds and reactions involved.⁽⁷⁾ Since sulfur is the major impurity in petroleum, the general technique is frequently called Hydrodesulfurization (HDS) in the industry.** However, the hydrogen reacts with other species besides sulfur compounds. For example, nitrogen compounds break down to liberate ammonia from the oil. This is called

* The most widely-used catalysts are composites comprised of cobalt oxide, molybdenum oxide, and alumina, where alumina is the support carrying the other agents as promoters. However, other catalyst materials are in use or under development. Much of the catalyst technology is proprietary, but the patent literature is extensive. Ranney⁽⁶⁾ has compiled information from over 200 patents during the period 1970-1975.

** A discussion of collection and processing techniques for the evolved H₂S will be found in Appendix B.

Table 2-2

CHEMISTRY OF HYDRODESULFURIZATION REACTIONS IN
PETROLEUM CRUDE OIL (7)

Name	Structure	Typical reaction
Thiols (mercaptans)	$R-SH$	$R-SH + H_2 \longrightarrow RH + H_2S$
Disulfides	$R-S-S-R'$	$R-S-S-R' + 3H_2 \longrightarrow RH + R'H + 2H_2S$
Sulfides	$R-S-R'$	$R-S-R' + 2H_2 \longrightarrow RH + R'H + H_2S$
Thiophenes		 + $4H_2 \longrightarrow n-C_4H_{10} + H_2S$
Benzothiophenes		 + $3H_2 \longrightarrow CH_3CH_2$  + H_2S
Dibenzothiophenes		 + $2H_2 \longrightarrow$  + H_2S

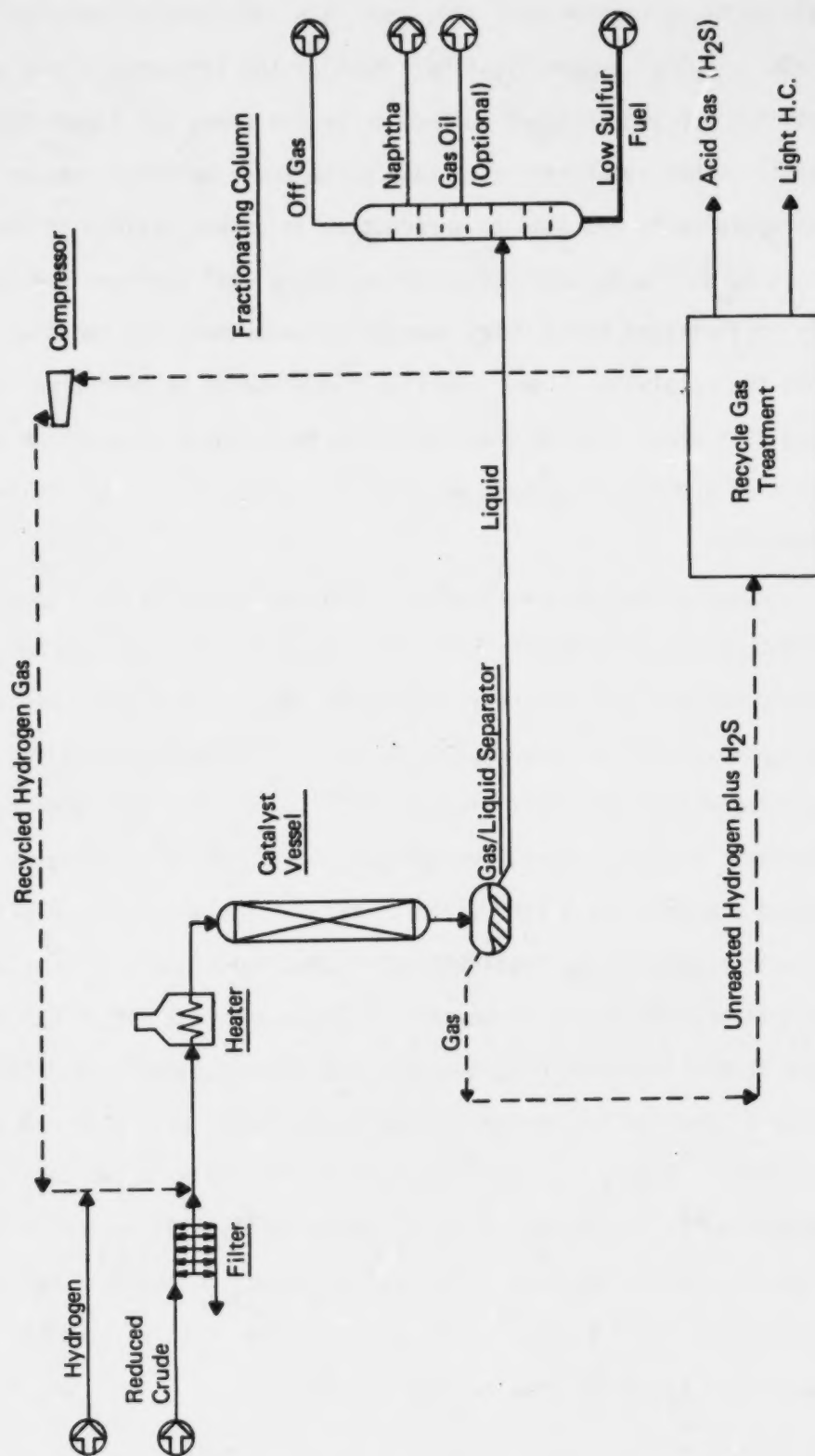
Used with permission Taken from: Hastings, K. H. and R. P. Van Drisen,
 "Hydrodesulfurization of Petroleum Crude Oil Fractions and Petroleum Products,"
Energy Technology Handbook, D. M. Considine, Ed., McGraw-Hill Book Co., 1977,
 p. 2-254.

denitrogenation or denitrification. The nickel and vanadium in the oil, which are bound as organo-metal compounds, are liberated by reaction with the hydrogen. This is called demetallization. Most of the liberated metals deposit (as the sulfide) on the catalyst surface or in its pores and slowly deactivate the catalyst. Other reactions which take place break up large complex molecules such as asphaltenes and lead to a reduction in carbon residue of the product oil.

By utilizing catalysts, the reactions with hydrogen can be restricted largely to the types above which take place under moderate reaction conditions. Without the catalysts, higher reaction temperatures or pressures would be required, and this would lead to greatly-increased hydrogen consumption due to hydrogenation of aromatic ring systems which are abundant in high boiling petroleum fractions.

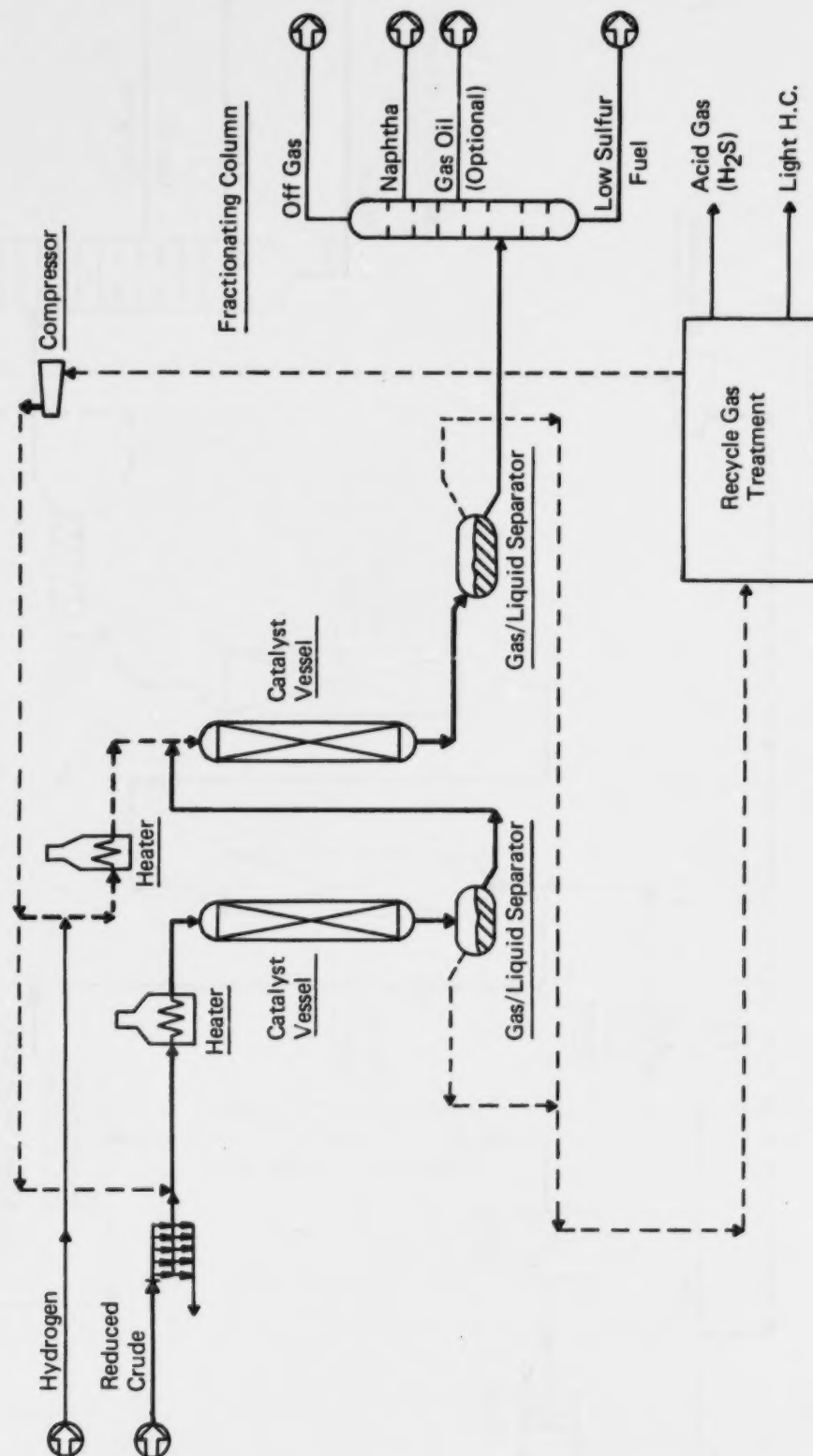
Many companies are engaged in developing and using catalytic hydro-treating (or hydrosulfurization) processes. All are similar in basic concept and vary only in details such as catalysts, process conditions, and complexity. A recent paper by Gulf Oil Company investigators traces the development of one basic process.⁽⁸⁾ Figure 2-2 illustrates the simplest commercial version currently marketed by Gulf, and it is known as Gulf II. Its basic elements are a feed filter, heater, single-stage catalytic reactor, a gas/liquid separator, a fractionating column, and a gas treatment section. This simple process system is capable of producing fuel oil of approximately 1% sulfur from a feedstock such as atmospheric resid containing 2-4% sulfur. To produce a lower sulfur content product, additional catalytic reaction stages must be added. Figure 2-3 shows the Gulf III system with two catalytic reaction stages which can produce fuel of approximately 0.3% sulfur content from the same feedstocks as above. The most advanced process Gulf has developed is known as Gulf IV (Figure 2-4). It uses three catalytic reactors and can produce fuel oils of approximately 0.1% sulfur.

Figure 2-2
BASIC HDS PROCESS (GULF HDS - TYPE II) (8)



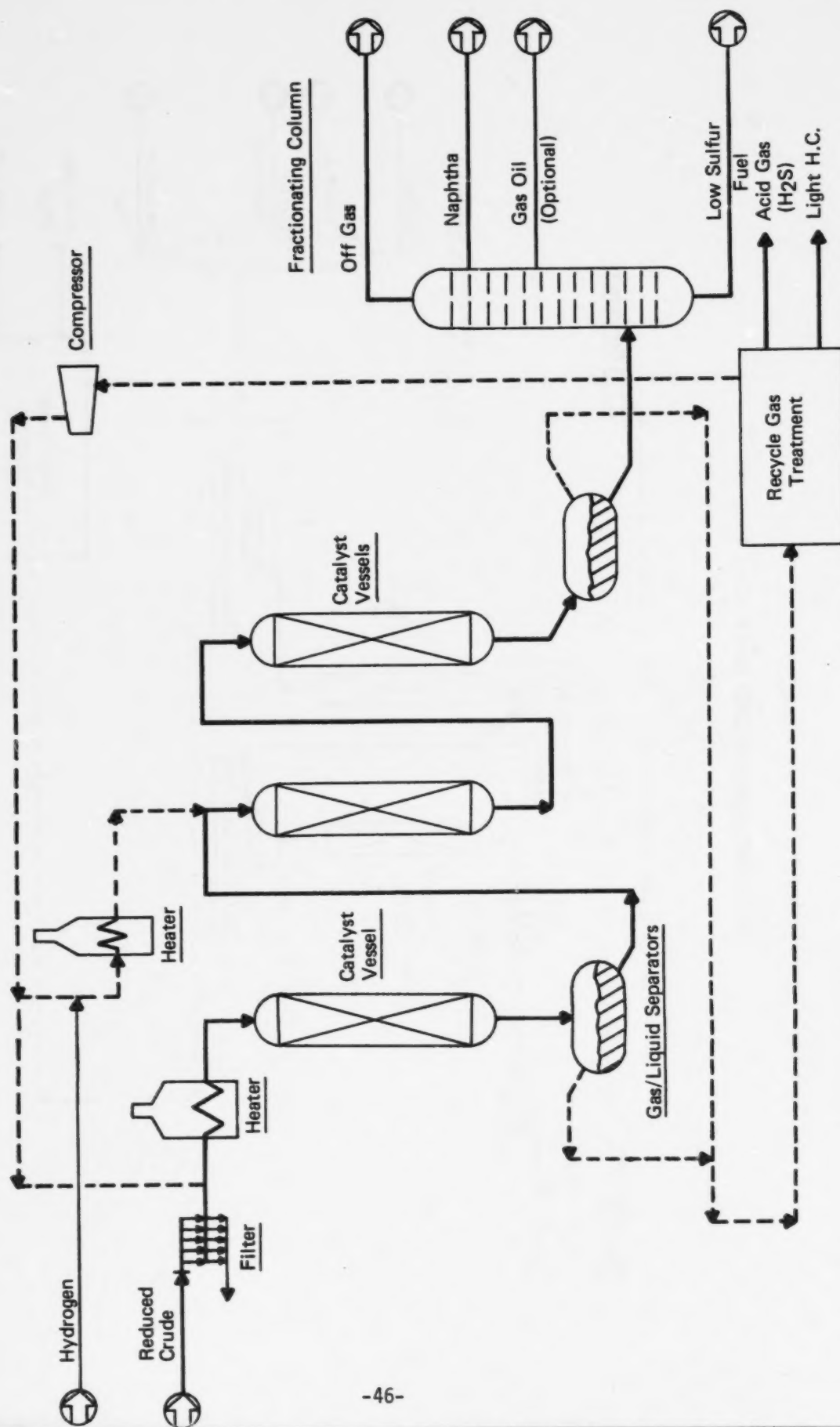
Used with permission Taken from: Frayer, J. A., et al., "Gulf's HDS Processes for High Metal Stocks," presented at the Japan Petroleum Institute, Tokyo, Japan, May 8, 1975.

Figure 2-3
IMPROVED HDS PROCESS (GULF HDS - TYPE III) (8)



Used with permission Taken from: Frayer, J. A., et al., "Gulf's HDS Processes for High Metal Stocks," presented at the Japan Petroleum Institute, Tokyo, Japan, May 8, 1975.

Figure 2-4
STATE OF THE ART HDS PROCESS (GULF HDS-TYPE IV)⁽⁸⁾



Used with permission Taken from: Frayer, J.A., et al., "Gulf's HDS Processes for High Metal Stocks," presented at the Japan Petroleum Institute, Tokyo, Japan, May 8, 1975.

Table 2-3 illustrates the typical product properties obtained when the three versions of the Gulf process are applied to Kuwait atmospheric resid containing 3.8% sulfur.⁽⁹⁾ It can be seen that the number of catalyst stages strongly affects both physical and chemical properties of the product oil. In addition to sulfur removal, other changes are noted: reduction in pour point and viscosity; and reduction of chemical impurities such as nitrogen, metals, salts, and ash.

There is a price to pay for such beneficial changes, however. The amount of hydrogen consumed increases with the degree of desulfurization. So does catalyst cost. A further cost is a slight reduction in heating value per gallon. Even though heating value/pound increases with the degree of desulfurization, the density of the product decreases; thus, slightly greater volumes of cleaned fuel oil must be burned to produce the same amount of heat provided by an untreated residual oil. The change in heating value is of the order of 1-3% on atmospheric resids and about 5% on vacuum resids. When the degree of clean-up is considered, this energy impact seems insignificant.

The composition of the feedstock to a hydrotreater strongly influences the amount of hydrogen and catalyst consumption in the process. Nelson⁽¹⁰⁾ has correlated hydrogen consumption with sulfur reduction for a variety of resid feeds. Figure 2-5 illustrates his results on feedstocks varying from 4-18⁰API gravity. It can be seen that to obtain 90% reduction in sulfur for an 18⁰API feedstock, about 650 scf of hydrogen are consumed per barrel of oil processed; whereas, a 4⁰API feed would require 1200 scf/barrel. Another of Nelson's correlations is shown in Figure 2-6, wherein he has plotted hydrogen consumption data for typical low metals atmospheric resid (16⁰API) and vacuum resid (6⁰API) as a function of sulfur desired in the fuel oil product. Thus, in producing 0.3-1.0% sulfur fuel oils from atmospheric resid, 345-775 scf of hydrogen per barrel are required, while vacuum resid requires 870 to 1150 scf to accomplish the same task.

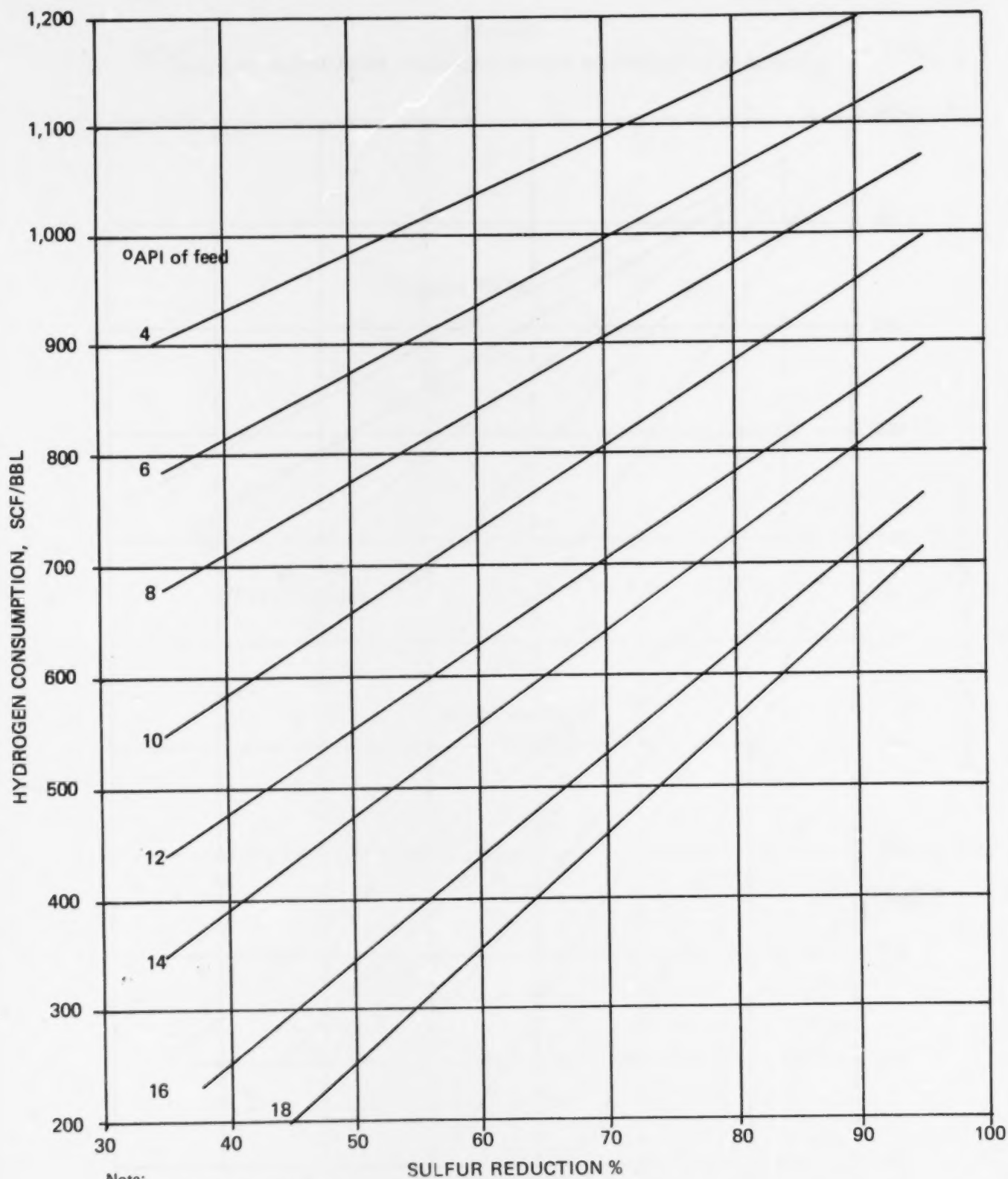
TABLE 2-3. TYPICAL PROPERTIES OF LSFO PRODUCT FROM GULF HDS PROCESSES⁽⁹⁾

	<u>Untreated</u>	<u>Gulf II</u>	<u>Gulf III</u>	<u>Gulf IV</u>
Product Yield: Vol. %	--	89.4	97.5	97.1
Product Properties:				
Cut Point: °F	650	650	375	375
Gravity: °API	16.6	20.0	23.4	24.1
Sulfur: Wt. %	3.8	1.0	0.3	0.1
Carbon Residue: Wt. %	9.0	5.31	3.33	2.75
Nitrogen: Wt. %	0.22	0.13	0.13	0.09
Nickel: PPM	15.0	4.6	1.3	0.4
Vanadium: PPM	45.0	8.2	2.2	1.0
Viscosity: SUV (210°F)	250	107.3	52	45
Ash: Wt. %	0.02	0.004	0.003	0.003
Salt: PPM*	44.9	0	0	0
Heat of Combustion: Btu/LB	**	19,110	19,250	19,375
Hydrogen: Wt. %	**	12.1	12.5	12.7
Carbon: Wt. %	**	86.7	87.1	87.1
Pour Point: °F	**	+60	+35	0
Hydrogen Consumption: SCF/BBL	--	497	663	812

* Salt refers to all water-soluble cations, determined as halide and reported as NaCl before desalting.

** Not stated.

Figure 2-5
CHEMICAL HYDROGEN CONSUMPTION IN DESULFURIZATION OF RESIDUA (10)

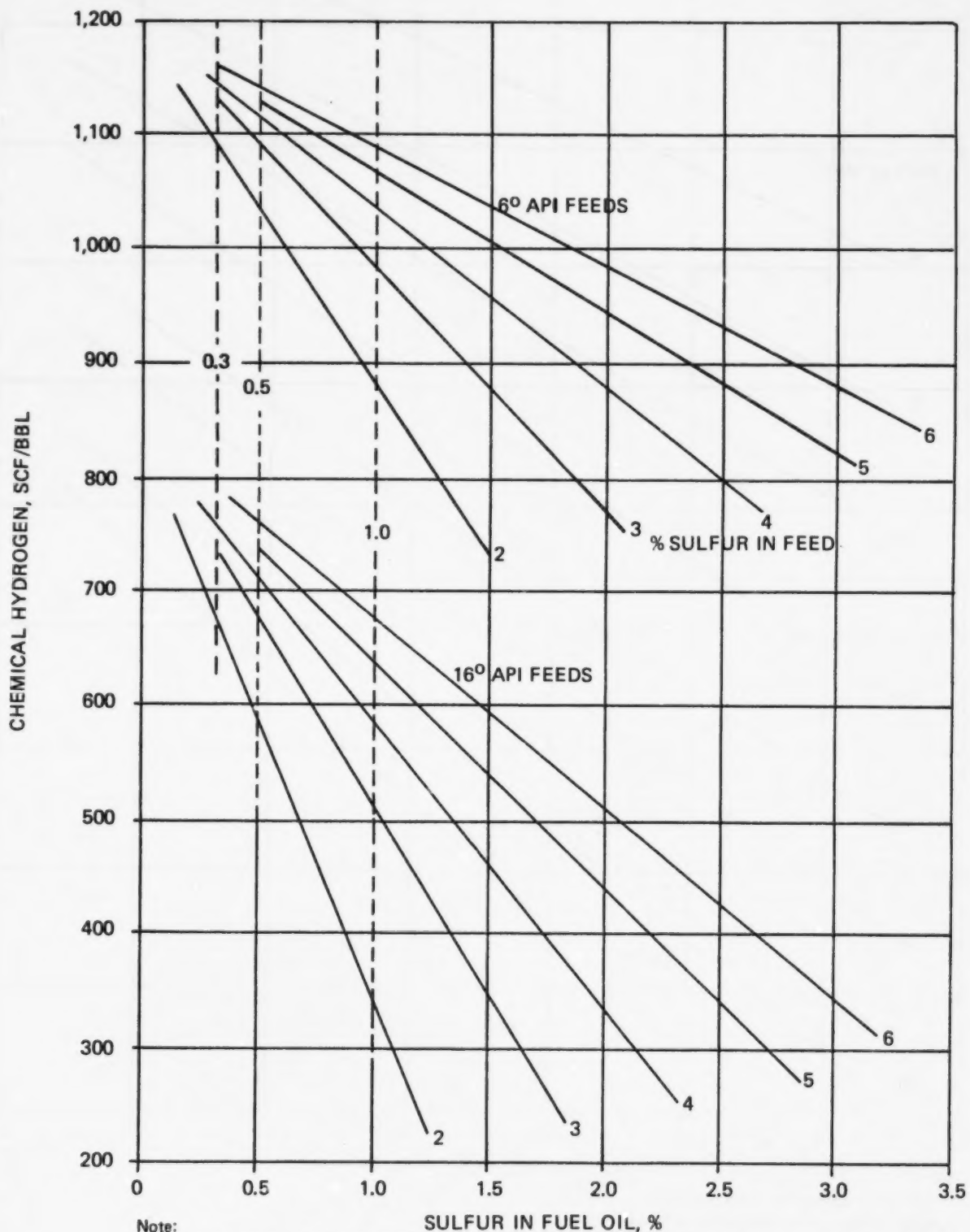


Note:

1. Reduce by 9% for fixed-bed processes.
2. Apply correction for high-metals feeds.

Figure 2-6

HYDROGEN CONSUMPTION FOR ATMOSPHERIC AND VACUUM RESIDUA ⁽¹⁰⁾



Note:

1. Reduce by 9% for fixed-bed processes.
2. Apply correction for high-metals feeds.

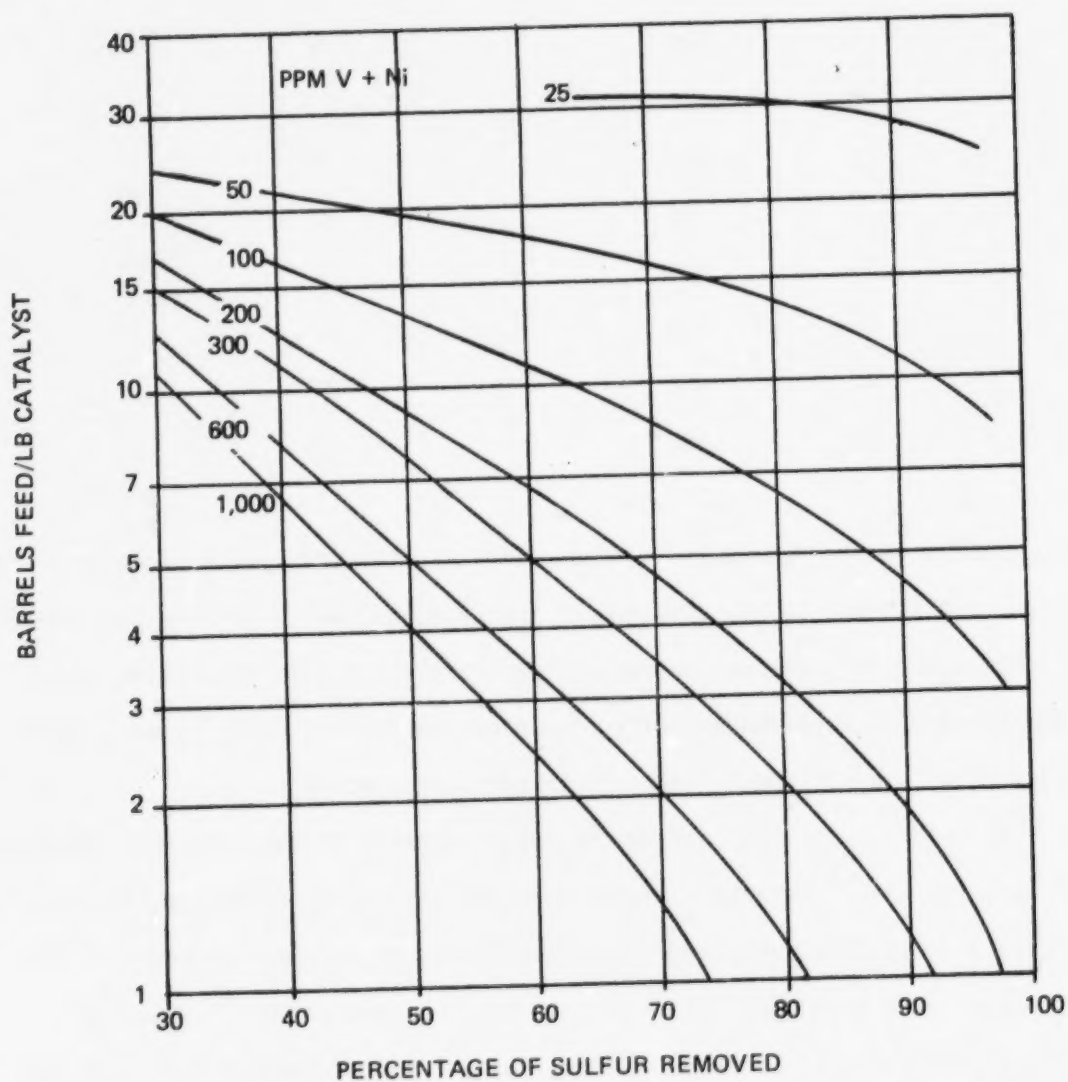
Both figures are based on normal metals content of less than about 200 ppm. Nelson suggests the following corrections to Figure 2-6 for higher metals content feedstocks:

<u>V + Ni,</u> <u>ppm</u>	<u>Corrections,</u> <u>%</u>
0-100	-2
200	+1
300	2.5
400	4
500	6.5
600	9
700	12
800	16
900	21
1000	28
1100	38
1200	50

The problem caused by metals is deposition onto the catalyst surface or in the pores. This leads to deactivation of the catalyst, which is only overcome by a temperature or pressure increase to maintain acceptable processing rates. The increase in required severity of process conditions leads to more hydrocracking with a subsequent increase in hydrogen consumption.

A further complication from the metals content of the feed is a shortening of catalyst life. Even though some deactivation can be tolerated, the resultant increase in hydrogen uptake means catalyst must be changed out sooner. The effect of metals can be seen in another Nelson correlation⁽¹¹⁾ shown in Figure 2-7. It will be observed that, for 90% sulfur removal from a 25 ppm metals content feedstock, about 27 barrels of oil can be processed per pound

Figure 2-7
EFFECT OF METALS ON CATALYST CONSUMPTION⁽¹¹⁾



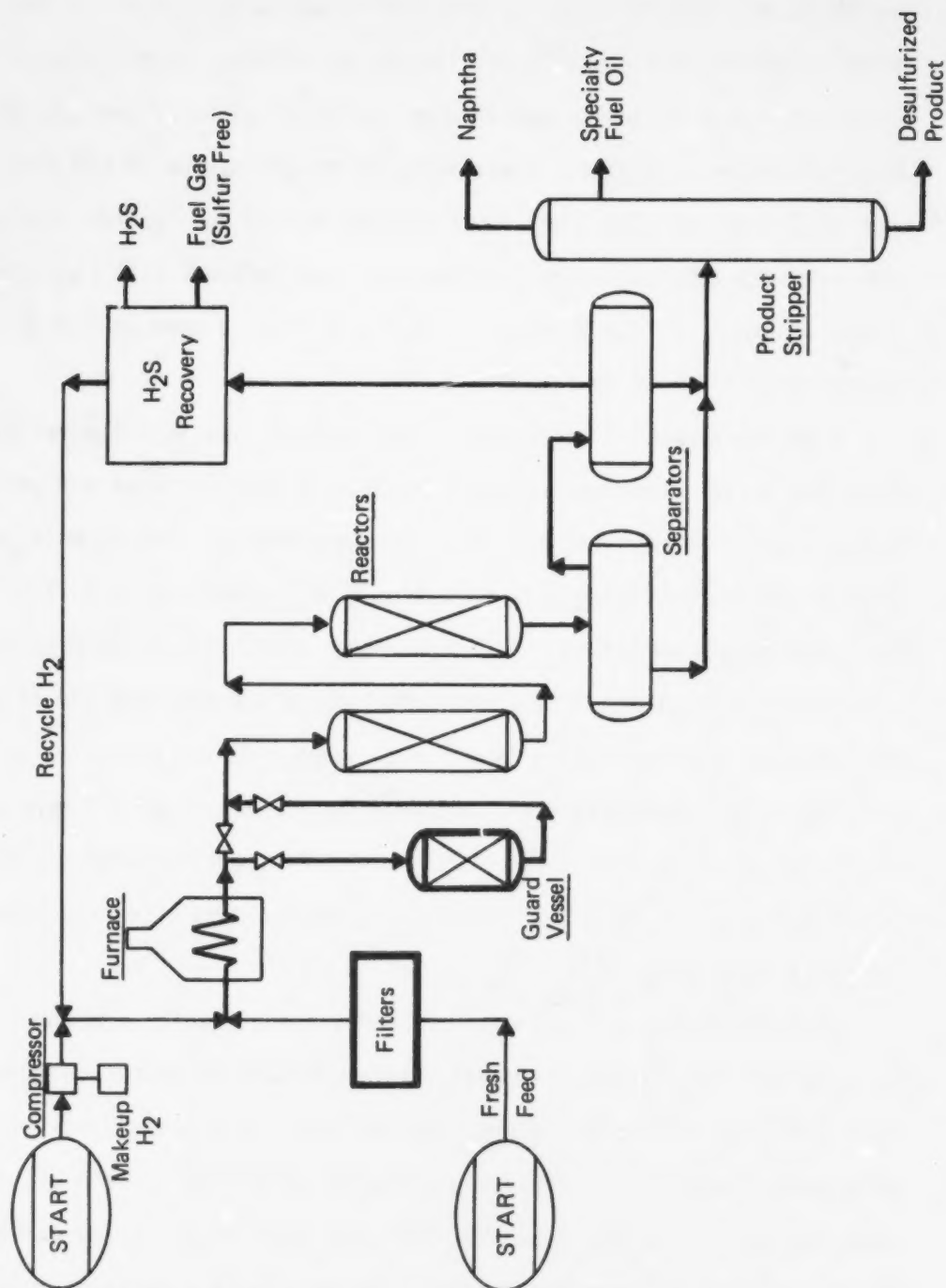
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of catalyst; to achieve the same sulfur performance with a 100 ppm metals content feedstock, only 4.5 barrels can be processed per pound of catalyst; a 300 ppm feedstock requires almost 1 pound of catalyst per barrel. Clearly, high metal feedstocks are a costly problem to the refiner. Most refiners are using a separate stage of lower cost catalyst material prior to the special hydrodesulfurization catalysts. These separate stages may be packed with a material such as alumina or clay, which collects the metals and "guards" the subsequent high activity catalyst. For this reason, some refiners call this stage a "guard reactor" or "guard vessel." Such a process scheme used by Exxon (called RESIDfining) is shown in Figure 2-8.⁽¹²⁾

From the above, it is obvious that catalyst life is quite variable. In a fixed-bed system, catalyst changes are usually once or twice per year, depending on product requirement and feedstock composition. For example, with the Gulf IV system, producing 0.1% LSF0 from 3.8% S Kuwait Resid (97% HDS), a catalyst life of six months is the design base. Similarly, using Arabian Heavy with RESIDfining at 75% HDS, a catalyst life of 400-500 days can be achieved. The catalyst bed temperature is not a constant. As can be seen in Figure 2-9, note that a bed temperature rise of 80°F is reached after 400 days operation on resid and about 120°F shortly thereafter. This is usually the normal limit for catalyst life, and changeout is required to eliminate excessive hydrogen consumption.⁽¹²⁾

Most refiners use fixed catalyst beds, which require a process shutdown for catalyst replacement. However, there are some advocates of expanded or ebullated beds with intermittent catalyst feed and bleed systems to maintain continuous operation at relatively constant conditions. The H-Oil process developed by Hydrocarbon Research, Inc. and utilized by Cities Service is an example of such an operating system. The expanded bed operates as a back mix reactor with the entire bed at a constant temperature. Such a system is less

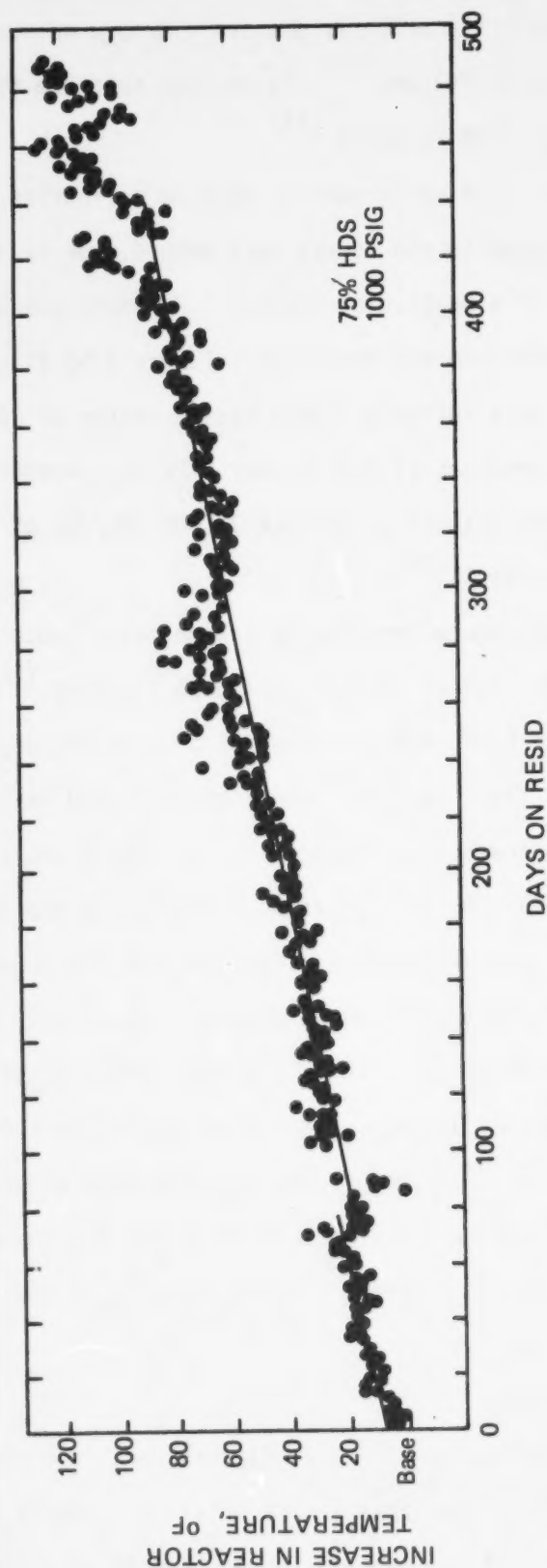
Figure 2-8
USE OF GUARD REACTOR (RESIDFINING PROCESS - SIMPLIFIED FLOW DIAGRAM)⁽¹²⁾



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Edelman, A. M., et al., "A Flexible Approach to Fuel Oil Desulfurization,"
presented at Japan Petroleum Institute, Tokyo, Japan, 8 May 1975, p. 5, and
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Figure 2-9
CATALYST BED TEMPERATURE VS. TIME (12)

LONG LIFE RUN
ARABIAN HEAVY ATMOSPHERIC RESID



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prone to plugging but has a slightly greater hydrogen consumption than a fixed bed system, according to Nelson.⁽¹⁰⁾ It is most suitable for high metals feedstocks where catalyst life is short.⁽¹¹⁾

Hydrotreating is applied in various ways in refineries.⁽¹²⁾ The direct approach is not necessarily the lowest cost method, nor is it best suited to the fuel oil market mix of a particular refiner. Refiners use both direct HDS processes, as well as indirect HDS processes. Figure 2-10 illustrates how a direct HDS process is used in a refinery. Note that a charge of 150,000 BBL/day of heavy Iranian crude produces 71,000 BBL/day of 2.5% atmospheric bottoms. This is fed to a RESIDfiner (Exxon) to produce 70,000 BBL/day of 0.3% sulfur fuel oil and 264 tons of sulfur.⁽¹²⁾

Figure 2-11 shows how a less costly scheme can produce a pool of fuel oils by desulfurization of lighter products and back blending.⁽¹²⁾ This is called indirect HDS. In the Exxon example shown, a 250,000 BBL/day charge of Arabian Light crude produced light gas oil, vacuum gas oil, and vacuum resid. Most of the light gas oil is treated by a hydrofiner to remove the sulfur. The vacuum gas oil is 95% desulfurized in a GO-finer. The vacuum resid stream is split; most is blended with the desulfurized light gas oil and vacuum gas oil to produce 0.3% S or 1.0% S fuel oils, while some is blended with light gas oil to produce 3.3% S bunker fuel oil. In this scheme, the refiner avoids the costly direct desulfurization of vacuum resid and yet satisfies three fuel oil market segments. He has taken advantage of the relative ease of desulfurization of light gas oil and vacuum or heavy gas oil which are low in metals content. The indirect scheme is limited in that it cannot produce as much very low sulfur oil as direct resid HDS can.

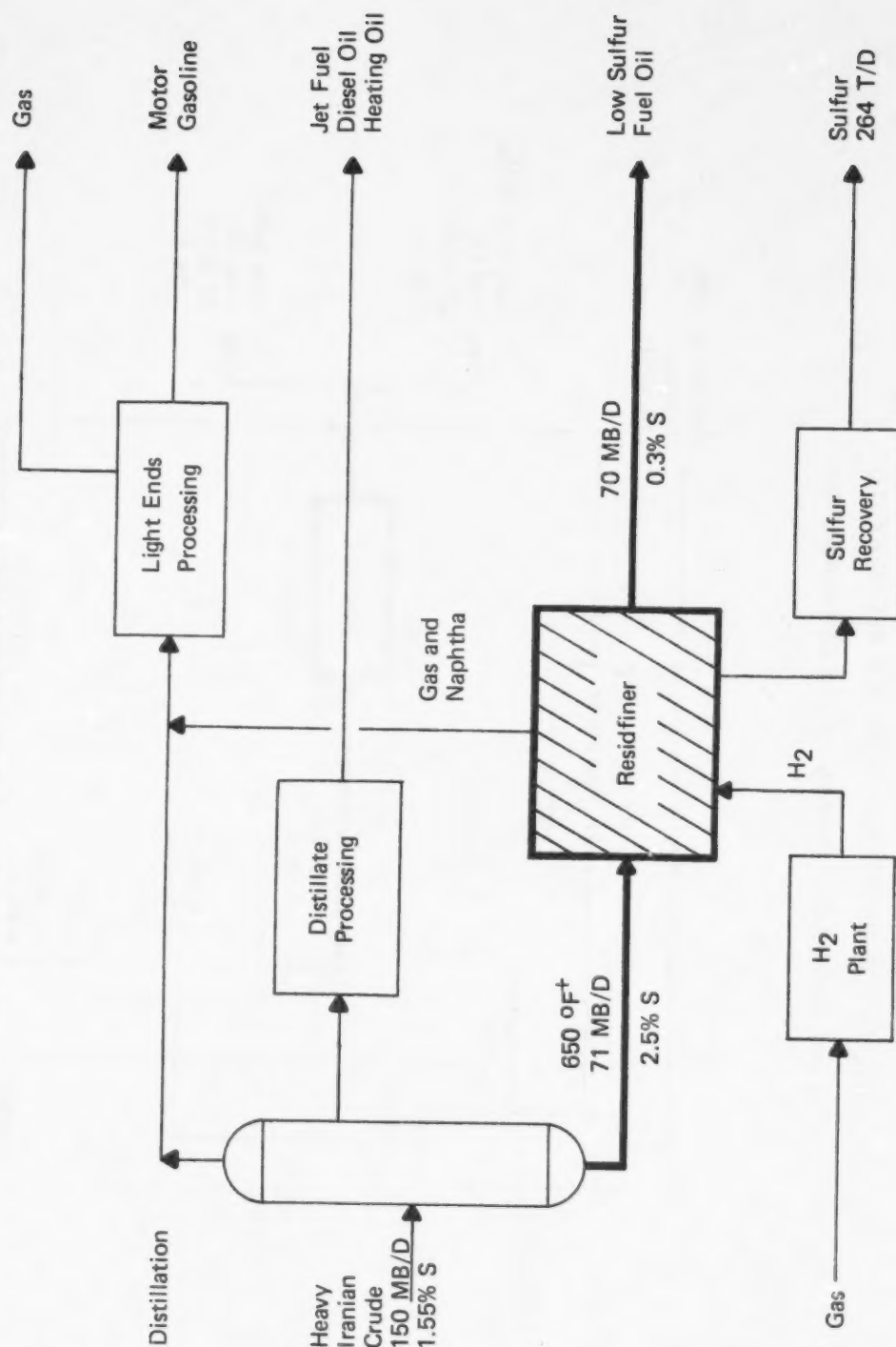
Development Status

Hydrotreating processing of heavy oils has been in commercial use for about 15 years.⁽⁷⁾ Most of the installed capacity is in Japan because of the extensive use of fuel oil for electric generation in that country and the very

Figure 2-10

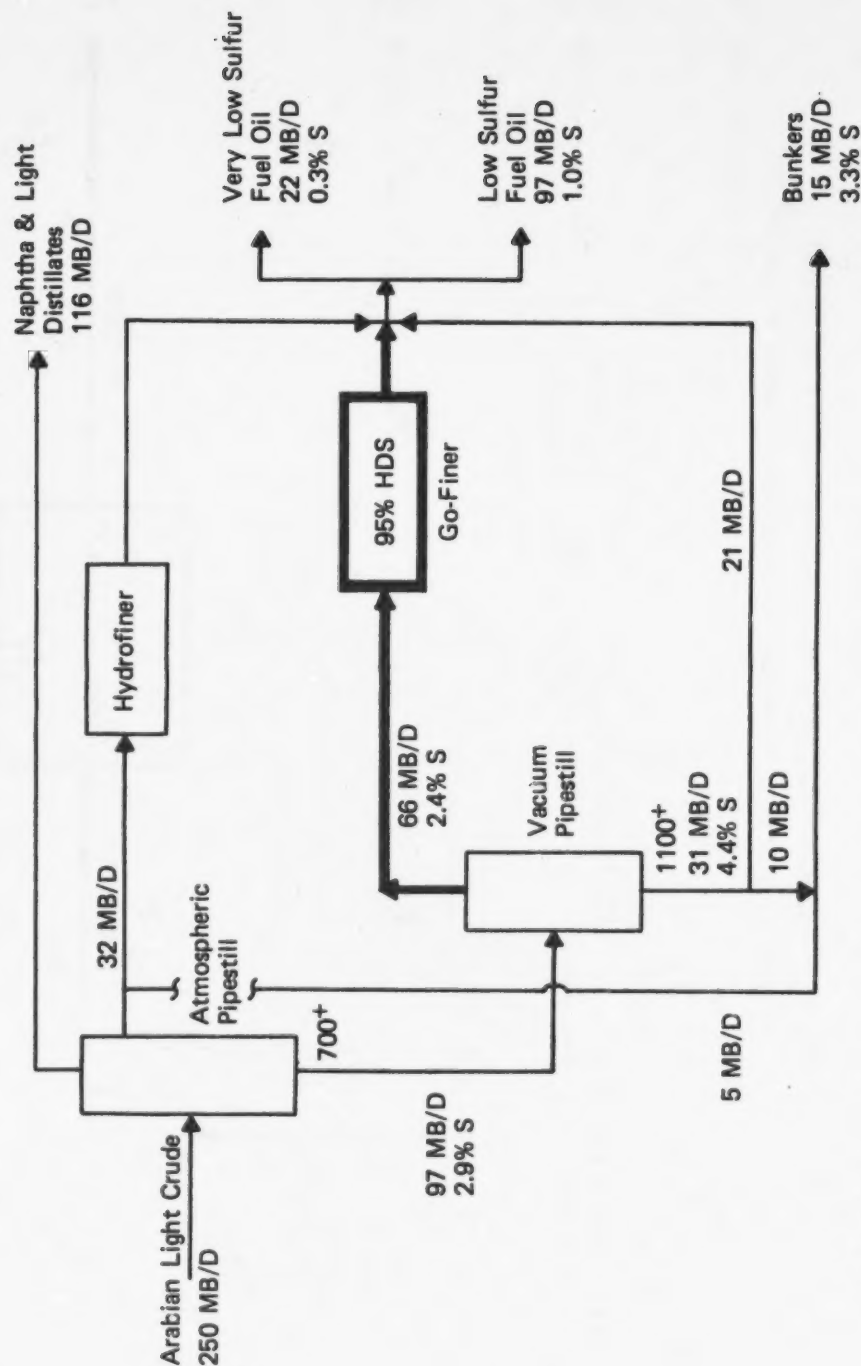
INTEGRATION OF DIRECT HDS INTO A REFINERY (12)

Typical Application of Residfining for Deep Desulfurization of Fuel Oil



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Figure 2-11
 UTILIZATION OF INDIRECT HDS IN A REFINERY (12)
 Typical Application of Gofining for Fuel Oil Desulfurization



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 presented at Japan Petroleum Institute, Tokyo, Japan, 8 May 1975, p. 5, and
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tight emission standards adopted by the Japanese government. Most of the processes were developed by U. S. oil companies, however, and built under license in Japan.

In recent years, desulfurization capacity has been installed in U. S. refineries to meet demand created by tightening air quality standards. As shown in Table 2-4, the current total U. S. refinery desulfurization capacity is over 1.8 million barrels per day from 86 plants.⁽¹³⁾ However, only 19 plants have direct catalytic resid or heavy gas oil hydrodesulfurization capability; and, they produce less than 0.6 million barrels per day. The other plants use physical or thermal cracking processes. Products are only slightly desulfurized when liquids are produced by visbreaking of gas oils. In coking processes, little or no fuel oil fraction is produced; i.e., gases, naphtha, and coke are generally the desired products. Gas oils produced are frequently recycled to the coker or are used as feed to catalytic cracking units for gasoline production, although they may be sold as low sulfur fuel oil.⁽¹²⁾

The extent of interest and process capability among refiners can be best appreciated by study of Table 2-5, which compiles commercial hydrodesulfurization results obtained by eleven companies.⁽¹⁴⁻²⁴⁾ The table shows the company which is the licensor of the process and its tradename, along with the results obtained with a variety of feedstocks from various crudes. Most of the data are on atmospheric resids, but there are also data on vacuum resids, vacuum gas oils, crudes, tar sands, and bitumen.

Applicability

Desulfurized oils are readily applicable to all boiler types and sizes. There seems to be no limitation on the use of refinery techniques as an emission control mechanism for SO_x , NO_x , and particulates on boilers which are currently burning fuel oils.

TABLE 2-4. SURVEY OF U. S. REFINERY DESULFURIZING CAPACITY - JANUARY 1978 (13)

	<u>No. Plants</u>	<u>Capacity</u>
Resid Desulfurizing	5	113,600 b/sd
Heavy Gas-Oil Desulfurizing	14	448,100 b/sd
Residual Visbreaking	-0-	-0-
Residual Upgrading	1	20,000 b/sd
Visbreaking	13	180,550 b/sd
Fluid Coking	6	134,100 b/sd
Delayed Coking	<u>47</u>	<u>936,000 b/sd</u>
Totals	86	1,832,350 b/sd

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TABLE 2-5. COMMERCIAL HDS RESULTS (14-24)

Licensor	Process Name	Feedstock			Product			Ref. No.
		Source	Type	V + N1 ppm/wt.	Sulfur Wt. %	Sulfur Wt. %	Desulf. %	H2 Cons. SCF/BBL
Chevron	RDS Hydrotreating	Arab Light	AR	38	32	0.46	86	560
		Arab Heavy	AR	115	3.9	0.55	85	750
	VRDS Hydrotreating	Arab Light	VR	38	4.1	1.0	76	780
		Arab Heavy	VR	115	5.1	1.0	80	960
C-E Lummus, Cities Service	LC-Fining	Kuwait	AR	64	4.0	1.4	65	520
		Kuwait	AR	64	4.0	0.4	90	690
		Gach Saran	VR	413	3.5	0.9	75	1400
		Arab Heavy	VR	195	4.9	1.2	75	1410
Exxon	GO-Fining	Arab Heavy	Crude	117	3.0	0.1	96	410
		Athabasca	Tar Sands	NR	4.0	0.1	97	975
		Kuwait	AR	66	3.0	0.3	90	280
		Arab Light	AR	40	2.3	0.23	90	220
-61-		Khafji	AR	105	2.9	0.3	90	300
		Gach Saran	AR	220	1.9	0.19	90	220
		Gach Saran	AR	220	2.5	0.3	88	625
		Arab Heavy	AR	120	4.2	0.3	93	915
Exxon	RESIDfining	Kuwait	AR	55	3.8	0.5	86	640
		Arab Light	AR	40	3.0	0.5	83	530
		Khafji	AR	105	4.0	0.5	88	700
		Gach Saran	AR	210	2.4	0.5	79	480
Gulf		Iran Heavy	AR	210	2.5	0.3	88	625
	Resid HDS (Gulf II)	Kuwait	AR	60	3.8	1.0	74	490
		Kuwait	VR	162	5.7	0.9	84	1250
		S. Louisiana	AR	5	0.46	0.05	87	
		W. Texas	AR	21	2.2	0.33	85	
		Kuwait	AR	66	3.8	1.0	74	515
		Khafji	AR	118	4.4	1.0	77	685
		Iranian	AR	183	2.5	0.65	74	440
		Kuwait	VR	199	5.7	0.9	84	1250
		Agha Jari	VR	274	3.8	0.75	80	1125
		Arab Light	VR	101	4.1	0.75	82	1000
		Kuwait	AR	60	3.8	1.0	74	630
		Mid East A	AR	40	3.0	0.6	80	490
		Mid East B	AR	114	4.2	0.8	76	655
		Mid East C	AR	110	5.8	1.5	74	820
		U. S. Domestic	AR	120	1.8	0.5	72	295

TABLE 2-5. COMMERCIAL HDS RESULTS (cont'd.)

Licensor	Process Name	Feedstock			Product			Ref. No.
		Source	Type	V + N1 ppm/wt.	Sulfur Wt. %	Sulfur Wt. %	Desulf. %	H2 Cons. SCF/BBL
Gulf	Resid HDS (Gulf III)	Kuwait	AR	66	3.8	0.3	92	770
		Kuwait	AR	66	3.8	0.5	87	660
		Khafji	AR	118	4.4	0.5	89	950
		Kuwait	AR	60	3.8	0.3	92	640
		Arab Light	AR	40	3.0	0.3	90	535
		Iran Light	AR	110	2.4	0.3	88	480
		Kuwait	AR	69	3.8	0.3	92	
		Kuwait	AR	60	3.8	0.5	87	815
		Mid East A	AR	40	3.0	0.3	90	720
		Mid East D	AR	114	4.2	0.5	88	825
		Mid East E	AR	116	4.6	0.7	85	965
		Kuwait	AR	60	3.8	0.1	97	700
		Kuwait	AR	60	3.8	0.1	97	720
		Kuwait	AR	66	3.8	0.1	97	960
		Kuwait	AR	60	3.8	0.1	97	960
Hydrocarbon Research/Cities Service	H-Oil	Ceuta	Crude	392	2.1	0.3	86	
		Athabasca	Bitumen	NR	4.9	1.0	80	1400
		Gach Saran	VR	413	3.5	1.0	71	1220
		Kuwait	AR	75	3.8	1.0	74	480
		Kuwait	AR	60	3.9	0.2	95	580
		Kuwait	VGO	N11	3.0	0.2	93	450
		Kuwait	AR	63	4.1	0.45	89	760
		Kuwait	VGO	N11	2.5	0.25	90	232
		Arab Light	AR	37	2.9	0.30	90	592
		Kuwait	AR	66	4.2	0.53	88	683
		Qatar	AR	35	2.8	0.23	93	536
		Kuwait	AR	66	4.2	0.58	86	747
		Kuwait	AR	66	4.2	0.62	85	753
		Iran Heavy	AR	179	2.7	0.37	86	626
		Iran Heavy	AR	179	2.7	0.38	86	707
Institute Francais du Petrole Nippon Oil Shell	Fuel Hydro- desulfuri- zation	Arab Light	AR	37	2.9	0.30	90	592
		Kuwait	AR	66	4.2	0.53	88	683
		Qatar	AR	35	2.8	0.23	93	536
		Kuwait	AR	66	4.2	0.58	86	747
Institute Francais du Petrole Nippon Oil Shell	Residual Oil Hydrodesul- furization	Kuwait	AR	66	4.2	0.62	85	753
		Iran Heavy	AR	179	2.7	0.37	86	626
		Iran Heavy	AR	179	2.7	0.38	86	707
		Iran Heavy	AR	179	2.7	0.38	86	707

TABLE 2-5. COMMERCIAL HDS RESULTS (cont'd.)

Licensor	Process Name	Feedstock			Product			Ref. No.
		Source	Type	V + N1 ppm/wt.	Sulfur Wt. %	Sulfur Wt. %	Desulf. %	H2 Cons. SCF/BBL
Shell	Residual Oil Hydrosulfurization	Kuwait	VR	130	5.2	1.14	78	845
		Kuwait	AR	66	4.2	0.57	86	747
		Arab Heavy	AR	115	4.3	0.80	81	749
		Iran Heavy	AR	179	2.7	0.34	87	760
		Qatar	AR	18	2.6	0.37	86	523
		Oman	AR	44	1.8	0.28	84	389
		Iran Heavy	AR	163	2.6	0.34	87	596
		Mid East	AR	50	4.2	0.5	88	725
		Kuwait	AR	46	3.8	0.3	92	730
		Gach Saran	AR	220	2.4	0.3	88	570
Union Oil UOP	Unicracking/HDS	N. Slope	AR	44	1.6	0.3	82	340
		Arab Light	AR	40	3.0	0.29	90	530
		Kuwait	AR	60	3.52	0.28	92	706
	RCD/Unibon							

AR = Atmospheric Resid

VR = Vacuum Resid

VGO = Vacuum Gas Oil

Factors Affecting Performance

Boiler performance is not strongly affected by using cleaner oils. As was discussed earlier, the reduction in heating value per gallon of 1-3% for atmospheric resid and perhaps 5% for vacuum resid is a mild penalty for the substantial improvement in emissions (see Section 2.3 below). This effect would be further offset by the greater ease of handling (lower pour point and viscosity) and by lessening of corrosion and deposit formation due to chemical composition changes in the oil as a result of hydrotreating.

2.3 PERFORMANCE OF CLEANED LIQUID FUELS IN INDUSTRIAL BOILERS

Emission Reductions

Sulfur oxides emissions are directly dependent on the sulfur content of the fuel. Hydrotreating techniques may be used to reduce sulfur content to the level required by emission standards. The NO_x emissions are generated from two sources: the nitrogen content of the fuel, and the nitrogen present from combustion air. The nitrogen content of the fuel can be reduced by hydrotreating. Thermal NO_x emissions are a function of boiler design and operation. Because of the smaller combustion chamber volume and reduced operating flexibility, the NO_x emissions from industrial boilers will be greater than those of utility boilers.⁽²⁵⁾⁽²⁶⁾ Similarly, due to the less efficient atomization and combustion in industrial boilers, particulate emissions are more directly related to the carbon residue of the fuel than to the ash content. Hydrotreating processes reduce carbon residue, thus reducing the particulate emission. Table 2-6 shows the effective sulfur, nitrogen, and carbon residue removal through several hydrotreating processes.⁽²⁷⁾⁽³⁸⁾⁽²⁹⁾⁽³⁰⁾ In general, the sulfur removal levels achieved have averaged approximately 80% by effectively reducing the sulfur content of fuel oils having 3% to 5% sulfur to levels of 0.5% to 1%. More stringent hydrotreating may even reduce the sulfur content of oils down to 0.1% sulfur.⁽¹⁷⁾ Approximately 40-50% nitrogen removal efficiencies are achieved by the best hydrotreating processes. This will result in a slight reduction of

TABLE 2-6. CONTAMINANT REMOVAL IN HYDROTREATING PROCESSES

Process	Feedstock		Weight % Sulfur			Weight % Nitrogen			Weight % Carbon Residue		
	Name	Gravity, °API	Feed- stock	Product	Removal	Feed- stock	Product	Removal	Feed- stock	Product	Removal
HDS-Gulf (27)	Kuwait	16.6	3.8	1.0	74	0.21	0.18	14	8.3	4.9	41
				0.5	87		0.14	33		4.0	52
				0.3	92		0.13	38		3.3	60
				0.1	97		0.11	48		2.2	73
RCD Unibon- UOP (28)	Kuwait	16.4	3.52	0.24	92	0.20	0.12	40	9.45	3.84	59
				0.3	88						
				0.3	93						
Residfining- Exxon (29)	West Tx. Sour West Tx. Sour		3.85 3.85	1.0	74						
				0.3	92						
Amoco (29)	Khafji Gach Saran	14.7 17.0	4.3 2.4	0.90	79	0.27 0.46	0.21	22			
				0.89	63		0.41	11			
Amoco (30)											

NO_x from industrial boilers burning the cleaned fuel. Greater nitrogen removal efficiencies will not significantly reduce the NO_x emissions from industrial boilers due to the large contribution of thermal fixation.

Hydrotreating of crudes reduces the ash content of residual oils by 80% (see Table 2-3), thus lowering particulate in the flue gas from combustion of these oils. All of these removal efficiencies are highly dependent on the type of feedstock, and the oil cleaning techniques should be evaluated on a case-by-case basis to determine the effective emission reduction.

Actual emission data from industrial boilers are shown in Figures 2-12, 2-13, and 2-14 for sulfur oxides, NO_x , and particulates, respectively. Figure 2-12 shows the direct relationship of sulfur content in the fuel with sulfur oxides emissions. Figure 2-13 shows the effect of reduced NO_x emissions by using a continuing lower nitrogen content. Figure 2-14 shows how particulate loadings can be reduced by burning fuels having a lower carbon residue content. These plots summarize the available emissions data on industrial boilers.⁽²⁴⁾⁽²⁶⁾⁽³¹⁾

Impact on the Boiler

There are or appear to be no significant negative impacts on the boiler operation. Burning lighter fuels will lower the severity of operation on the boiler. The modest effects (1-5%) on heat content per gallon will require additional fuel consumption to achieve rated boiler output.

2.4 GASIFICATION PROCESSES FOR PRODUCING CLEAN GASEOUS FUELS

Process Description

Gasification processes can convert high-sulfur feedstocks into a fuel gas by controlled partial oxidation (POX) with air or oxygen. No catalyst is required; thus, a wide range of fuels can be converted to clean gaseous fuels. The desalted feedstock is partially oxidized at high temperature to form a gaseous mixture of carbon monoxide (CO) and hydrogen (H_2) with a small amount of methane (CH_4). Carbon soot produced as a result of incomplete combustion is recycled back to the process. Either oxygen or air may be used for the partial

FIGURE 2-12
EFFECT OF FUEL SULFUR CONTENT ON SO₂ EMISSIONS

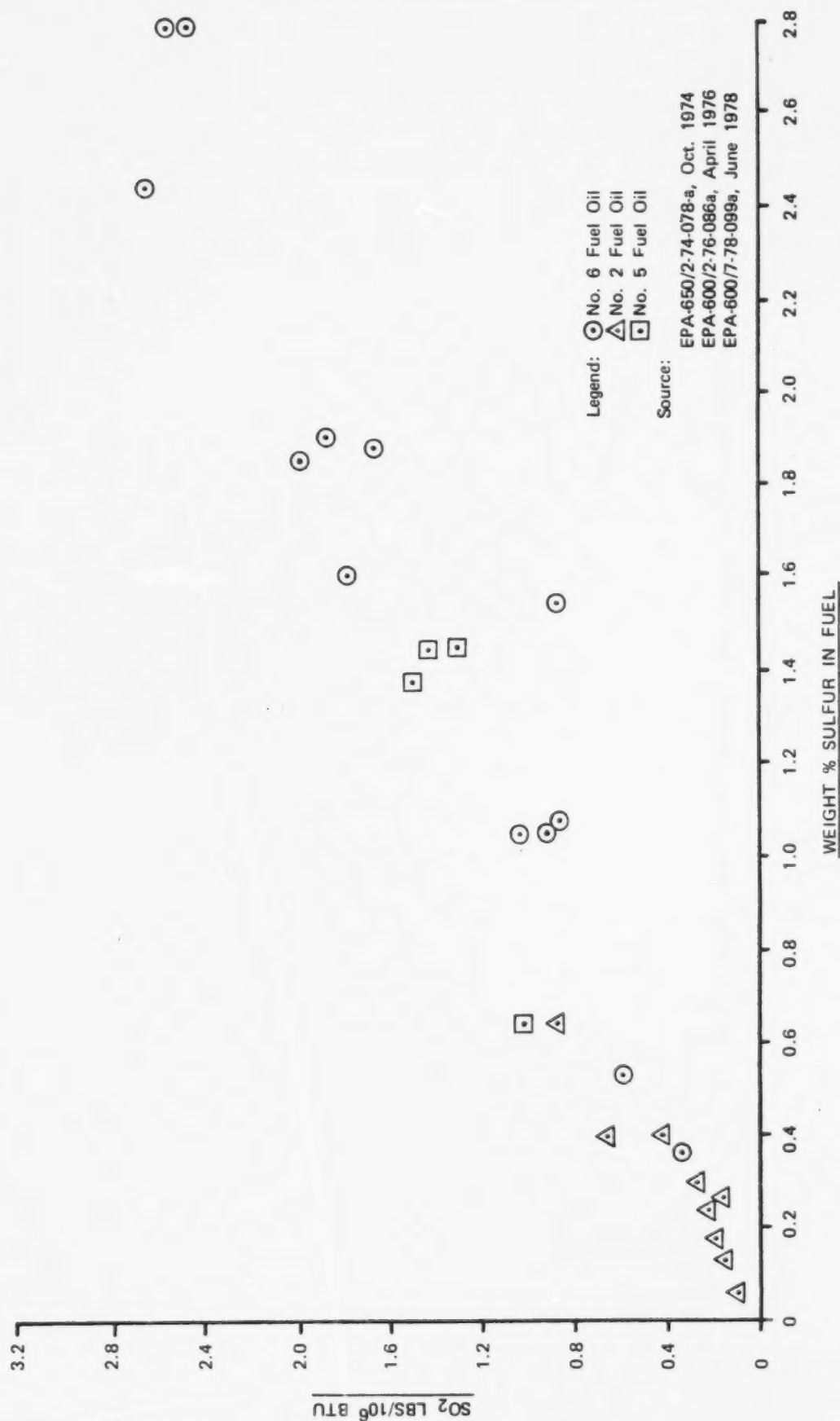


FIGURE 2-13

EFFECT OF FUEL NITROGEN CONTENT ON TOTAL NITROGEN OXIDES

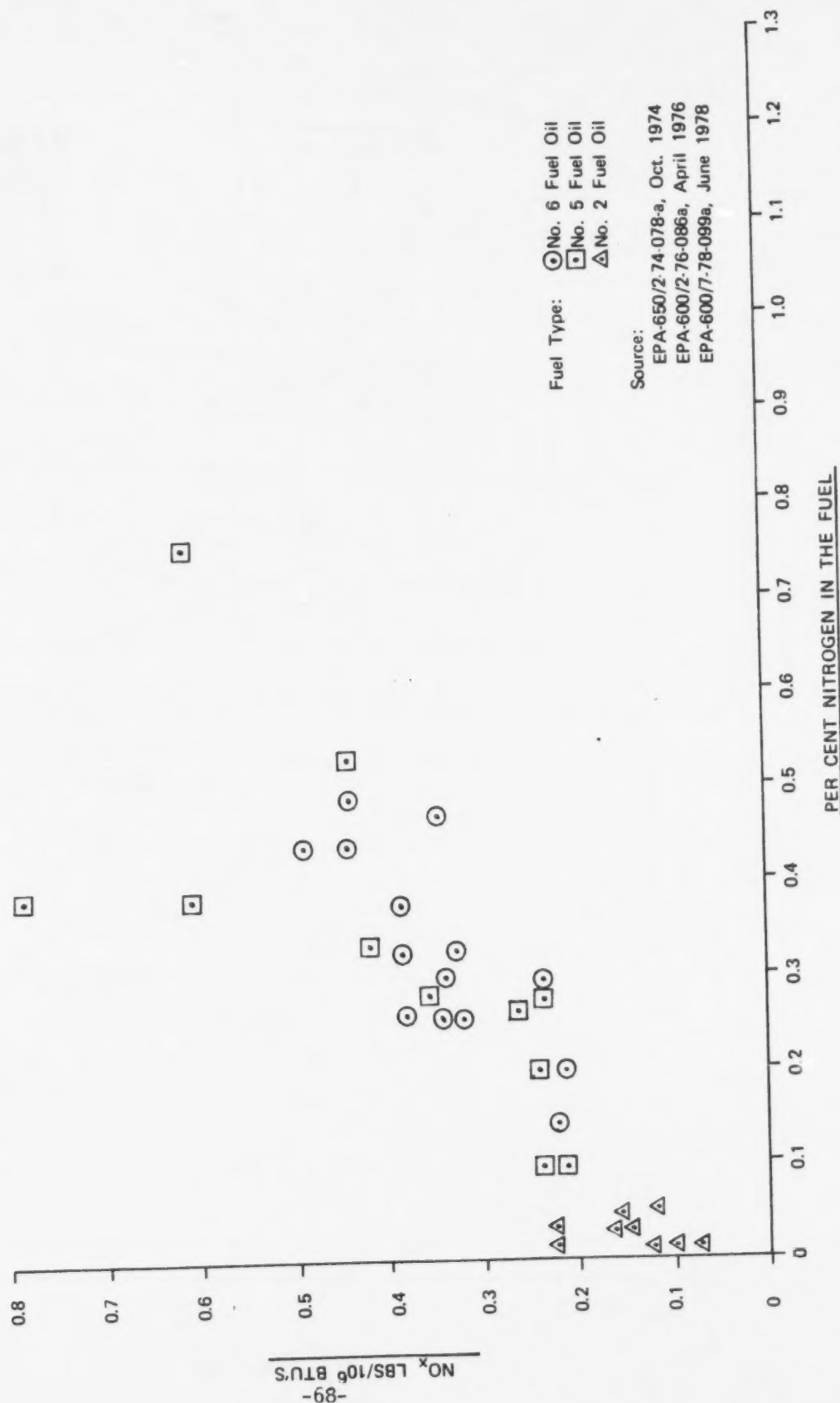
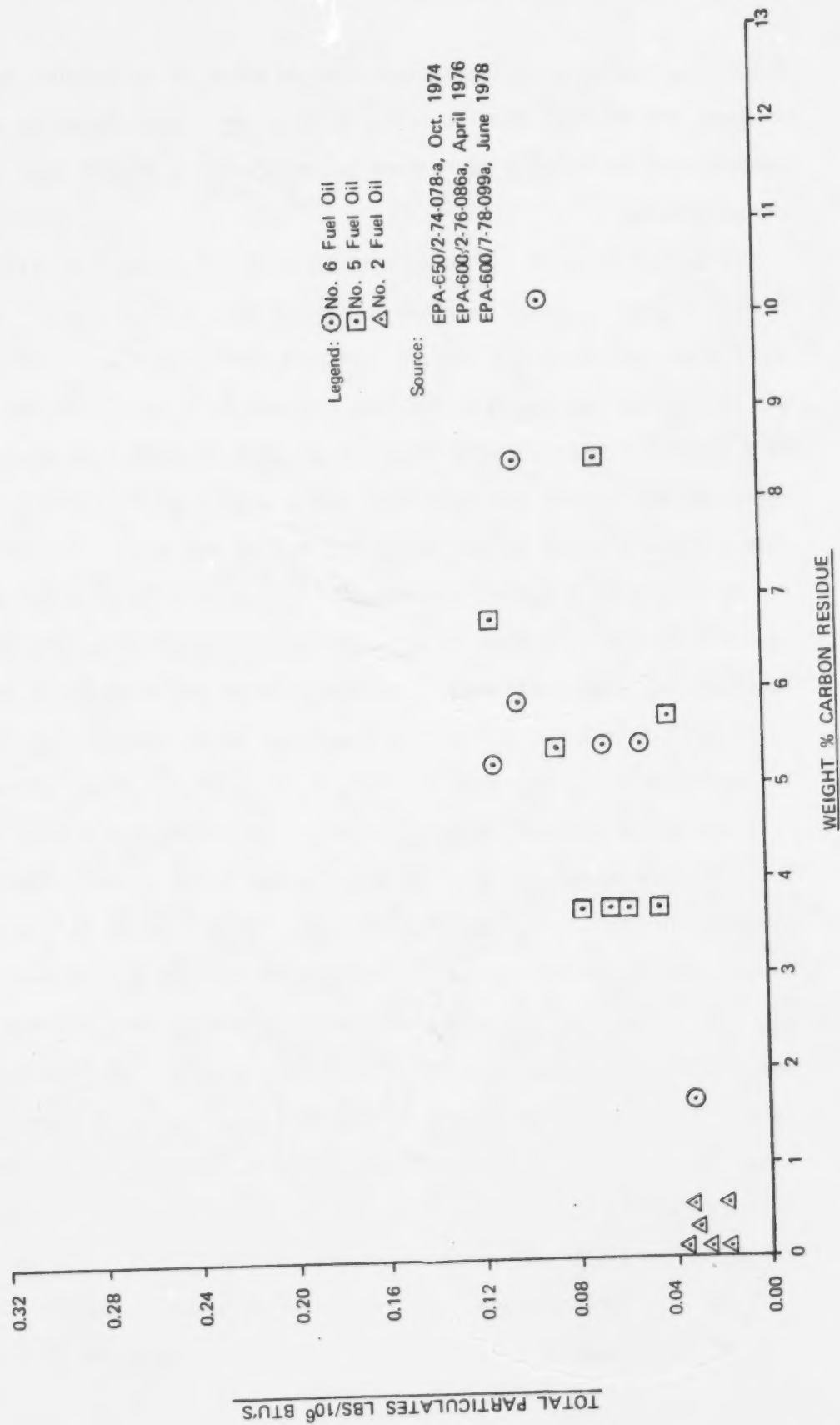


FIGURE 2-14

EFFECT OF FUEL CARBON RESIDUE CONTENT ON TOTAL PARTICULATE EMISSION



oxidation, depending on the desired heating value of the product gas. When air is used, the nitrogen remains in the product gas. When oxygen is used, the peak temperatures are usually controlled by introducing a diluent such as steam or carbon dioxide.

Figure 2-15 shows a flow diagram of a typical partial oxidation process.⁽³²⁾ In this process, a heavy residuum and the oxidant (air or oxygen) are preheated with steam and fed to the reactor. The hot reactor effluent [2400°F (1316°C)] gas containing some ash from the feed and soot (1-3% by wt. of fuel) is passed to a specially-designed waste heat boiler which produces high pressure steam. The crude gas exiting the waste heat system [about 325°F (163°C)] is then passed into a carbon removal system, which consists of two units. The bulk of the carbon is removed by a special carbon-water contactor of proprietary design; the remaining carbon is removed by a cooler/scrubber water wash. The product gas contains less than 5 ppm carbon and virtually no ash or other particulates. It is directly usable for gas-turbine fuel after sulfur removal (see Appendix B for a discussion of processes for removal of H₂S from hydrocarbon gases).

The carbon produced by gasification is collected as a slurry, dewatered, and recycled back to the process. In many systems in use, a pelletizing-homogenizing system is used to collect and recycle soot. This is shown in Figure 2-16.⁽³³⁾ If the oil feed is not too heavy, the carbon particles are preferentially coated with oil to form pellets which then can be separated from the water phase. The pellets are then ground up again after mixing with more oil feed and recycled to the gasifier. If very heavy feedstocks (such as pitch from propane deasphalting) are used, then the Shell Closed Carbon Recovery System (Figure 2-17) is needed. Naphtha is used to collect the carbon particles, which are then transferred to the oil feedstock in a stripping column.⁽³³⁾

The desulfurized product gas has a heating value of approximately 300 Btu/Scf when oxygen is used for the oxidation. By comparison, the product from

Figure 2-15

TYPICAL PARTIAL OXIDATION PROCESS FLOW DIAGRAM (SHELL GASIFICATION PROCESS) (32)

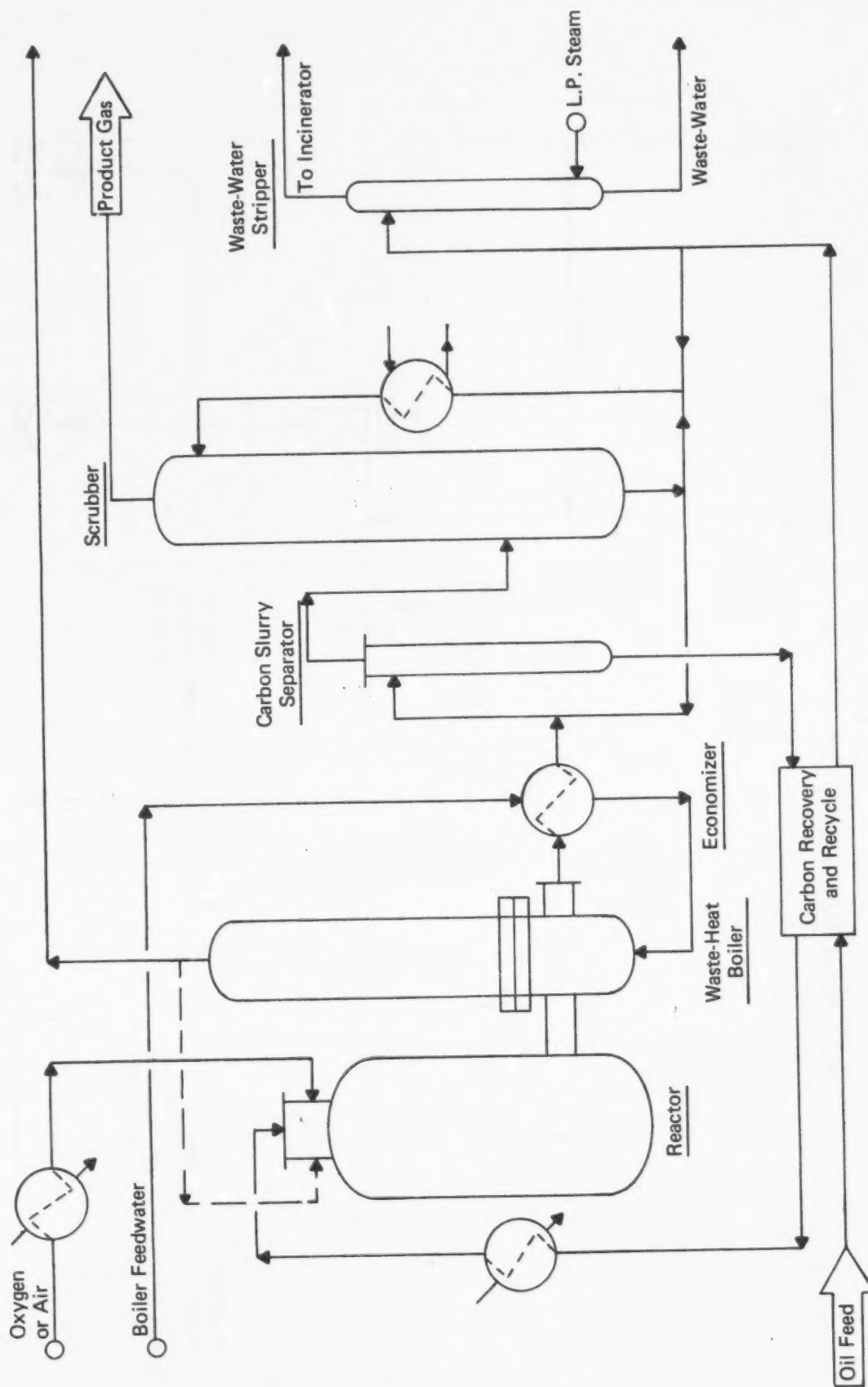


Figure 2-16
SHELL PELLETIZING SYSTEM FOR SOOT RECOVERY AND RECYCLE (33)

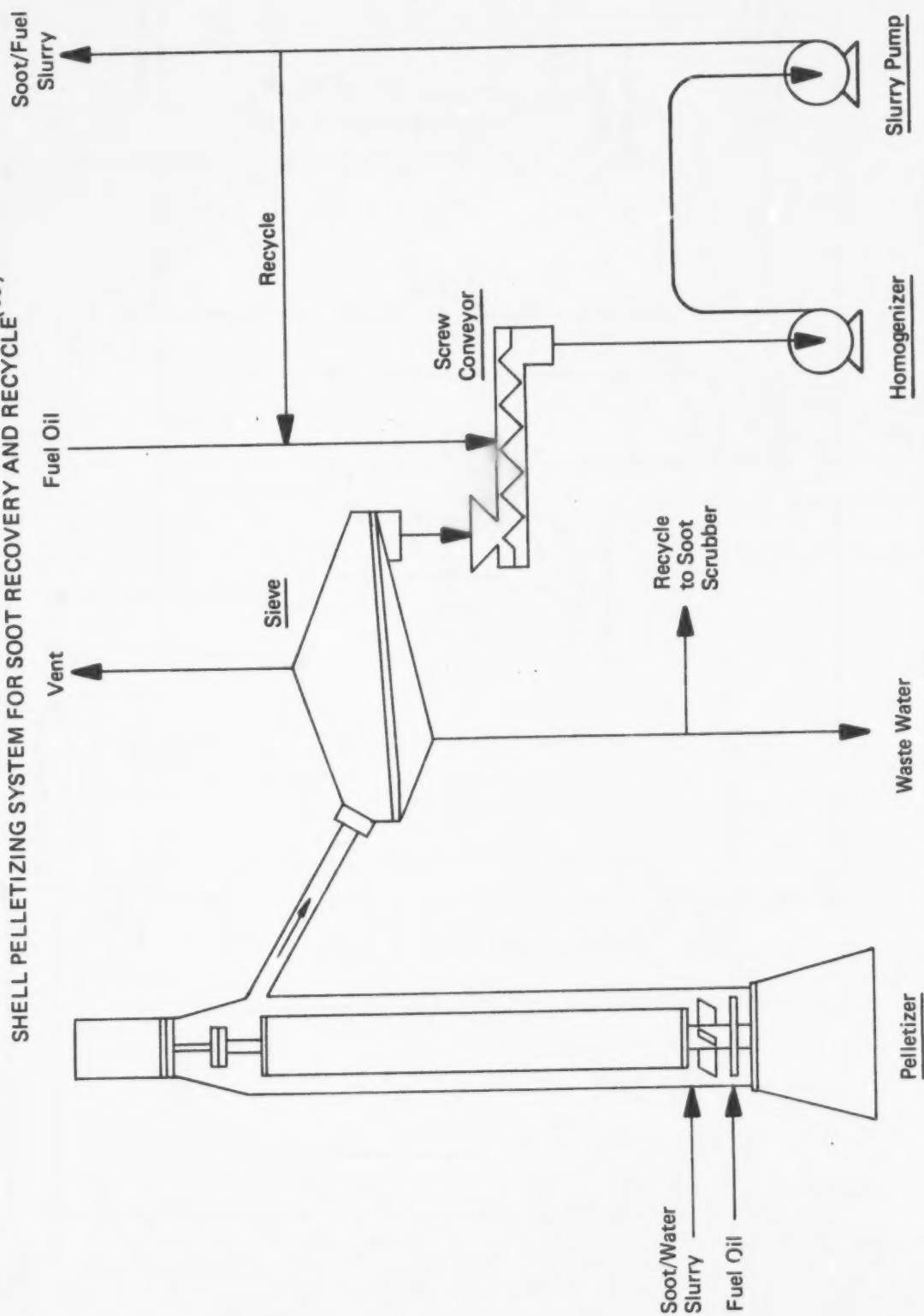
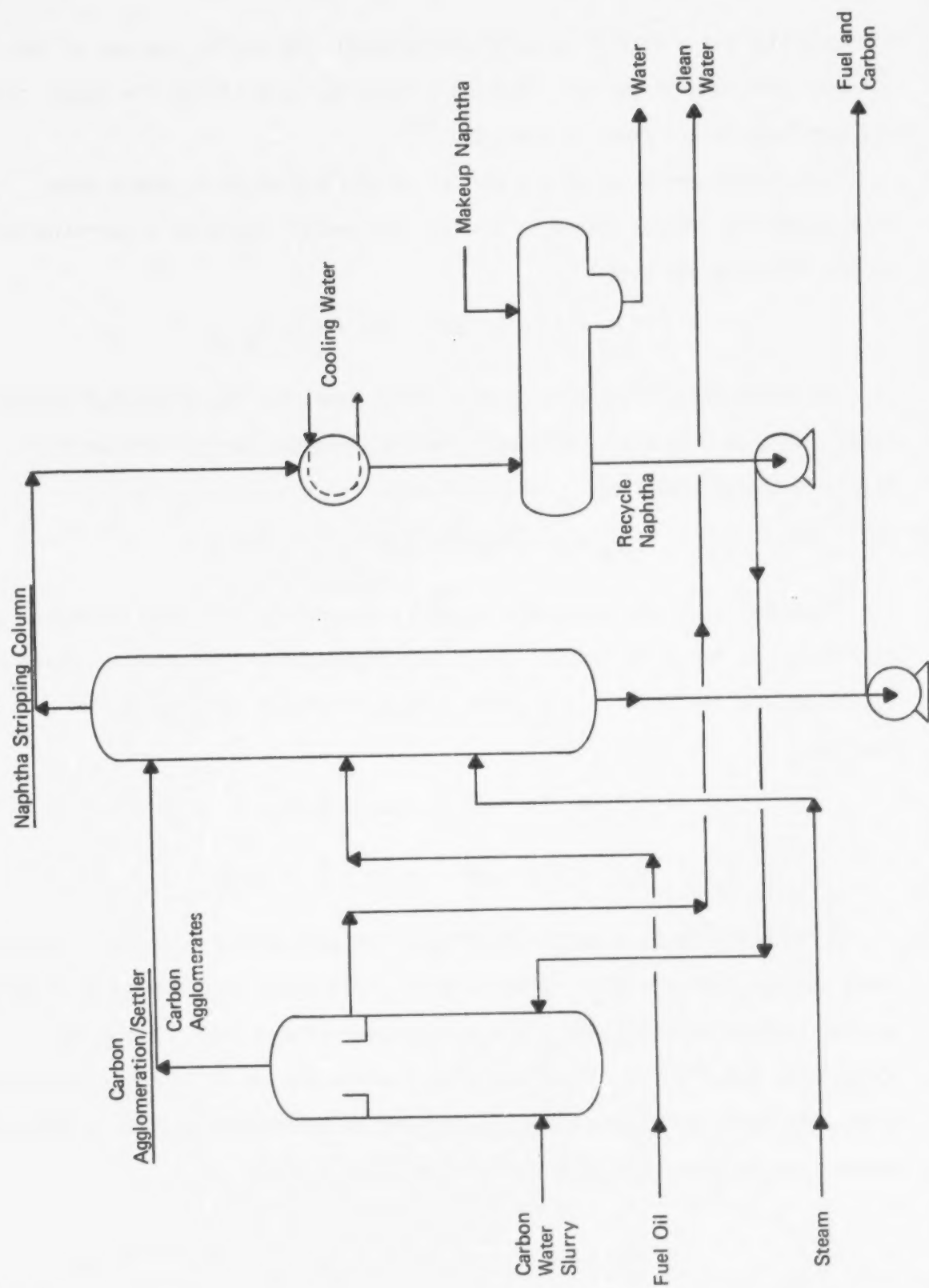


Figure 2-17
SHELL CLOSED CARBON RECOVERY SYSTEM (33)

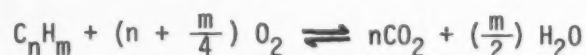


air oxidation has a heating value of approximately 120 Btu/Scf because of the nitrogen remaining in the gas. Typical product-gas compositions for oxygen and air gasification are shown in Table 2-7.⁽³²⁾

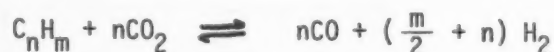
The process chemistry of the partial oxidation process is complicated, even though the process system is simple. The overall reaction is approximated by the following equation:



Following the initial heat-up phase where some cracking of the hydrocarbon takes place, part of the hydrocarbons react with oxygen during ignition in a highly exothermic reaction:



Practically all the available oxygen is consumed in this reaction whose equilibrium is far to the right. The remaining unoxidized hydrocarbons react with steam and the combustion products from reaction (2) via endothermic reactions:



The burner-reactor system is designed for good mixing to prevent excessive local temperatures and to bring the complex of reactions to a thermal equilibrium at 2350 to 2550°F (1288-1399°C) in a very short residence time. A soaking phase takes place in the rest of the reactor where the gas is at a high temperature. The final gas composition is determined by secondary reactions of methane, carbon, and the water-gas shift equilibrium.

TABLE 2-7. TYPICAL PRODUCT GAS COMPOSITION FROM GASIFICATION PROCESSES (32)

	<u>% vol., dry basis</u>	
	<u>O₂ oxidation</u>	<u>Air oxidation</u>
Hydrogen	48.0	12.0
Carbon Monoxide	51.0	21.0
Methane	0.6	0.6
Nitrogen	0.2	66.0
Argon	0.2	0.4
Sulfur *	<u>5 ppm</u>	<u>5 ppm</u>
Total	100.0	100.0

* after desulfurizing using Shell Sulfinol or ADIP process

Used with permission - Taken from: Kuhre, C. J. and J. A. Sykes, Jr.
Energy Technology Handbook D. M. Considine, Ed., McGraw-Hill Book
 Company, 1977 pages 2-173 & 2-174

These are slow reactions, and methane contents are higher than equilibrium calculations predict.

During the soaking phase, a portion of the carbon (soot) disappears, according to the reactions:



Some carbon is always present in the product gas from the reactor (approximately 1 to 3% of the oil feed), but generally soot is recycled to extinction.

The composition of the fuel gas is determined by the water-gas shift equilibrium:



which becomes fixed as the gas leaves the reactor at 2200 to 2400°F (1204 to 1316°C) and then is rapidly quenched in the waste heat boiler to about 325°F (163°C).

Development Status

Over 200 commercial partial oxidation reactors are in successful operation worldwide. (34) Two similar commercial processes are primarily in use: the Shell Gasification process and the Texaco Synthesis Gas Generation Process. Shell has supplied slightly more than half of the installed units. The commercial application of these gasification processes for producing clean gaseous fuels was introduced during the early 1950's. The total capacity of the installed partial oxidation units is unknown because of the wide ranges of product gases, ranging from ammonia to methanol to synthesis gas, and because of the variety in feedstocks currently being used.

A recent development partially funded by the EPA has resulted in the design, construction, and testing of the Chemically Active Fluid Bed (CAFB) process demonstration unit in San Benito, Texas. (35) The CAFB process is designed

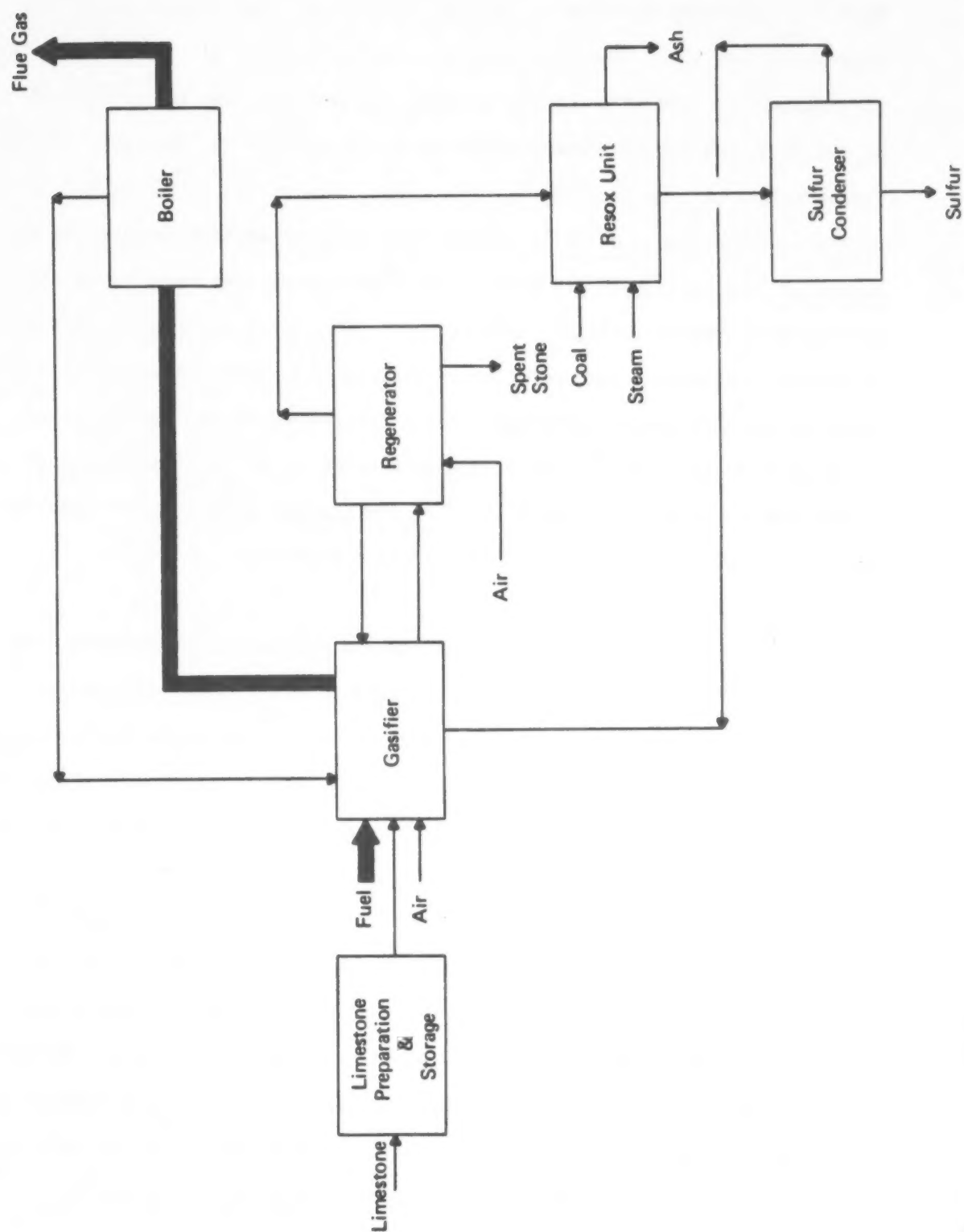
to produce a clean, low-sulfur gas by partially oxidizing a heavy, high-sulfur feed in a limestone fluid bed. Hydrogen sulfide and some organic sulfur are absorbed by the lime. The remaining hot, low-sulfur fuel gas produced is ready for combustion. The CAFB reactor contains two sections; one for gasification of the feed, and one for regenerating the sulfur-containing limestone. During regeneration, air reacts with the spent stone, freeing the sulfur as sulfur dioxide. The sulfur dioxide is removed from the regeneration gas and may be recovered in a variety of processes. The limestone is then recycled to the gasification section until it loses its efficiency as an absorbent. This unit is currently scheduled for operation in the summer of 1979. A schematic flow-sheet of the CAFB demonstration unit being constructed in San Benito, Texas, is shown in Figure 2-18,⁽⁹⁾ and a cutaway drawing of the CAFB gasification/regenerator is shown in Figure 2-19.⁽³⁶⁾ The San Benito unit is designed to use either coal (lignite) or residual oil as a feedstock.

Applicability

The gasification processes produce low- to medium-Btu gas products from liquid fuels. The low-Btu gas can be utilized in most, if not all, boilers designed for oil, coal, or gas. Modifications to the fuel burners are required for proper fuel/air control. Boiler development is progressing to the end that a wide variety of fuels may be utilized. However, derating of an existing boiler could result if the flue gas volume is increased in an existing boiler, the amount depending on the boiler design, e.g., with or without superheat.⁽³⁶⁾

It is probable that the smaller-size industrial boiler users would not find the CAFB useful, since additional capital expenditures and land space are required. There are no technical constraints to prohibit the use of the CAFB for any size industrial boilers, but an economic study needs to be made to determine the minimum size of boiler which would make the use of the CAFB process an attractive alternative to other control measures.

Figure 2-18. CAFB CHEMICALLY-ACTIVE FLUIDIZED BED PROCESS SCHEMATIC FLOW DIAGRAM⁽⁹⁾



or exchanger for high-temperature recovery, special design must be used to allow the carbon by-product to pass through the system without fouling. This fouling would reduce the amount of steam produced, thus reducing the efficiency of the process. One prototype unit has been in operation for nearly 20 years without requiring gas-side cleaning.⁽³²⁾

Particulate and ash carryover into the product gas are controlled by the slurry separator and water scrubber. Ash buildup in the reactor normally requires only an annual cleanout. Sulfur content of the product fuel gas is dependent on the feedstock sulfur content and the H_2S removal efficiency of the absorbent in the removal processes employed. An absorbent should be chosen that would also remove as much of the other traces of sulfur compounds, such as carbonyl sulfide and carbon disulfide, as possible. All of the sulfur compounds will normally form sulfur dioxide when the product gas is burned. Generally, greater than 99% removal of the sulfur compounds is readily achievable with the existing sulfur removal processes.⁽³⁸⁾

In the case of the CAFB, the sulfur content of the fuel gas is affected by the calcium-to-sulfur ratio in the fuel bed. With the integrated gasifier-regenerator, this ratio can be maintained within narrow operating limits. It is, therefore, thought that the SO_2 concentration in the CAFB product gas could be controlled within narrow limits by controlling the firing rate and the calcium-to-sulfur ratio in the fuel bed.

2.5 PERFORMANCE OF PRODUCT FUEL GASES ON INDUSTRIAL BOILERS

Emission Reductions

Sulfur oxide emissions from the combustion of fuel gas from gasification processes are directly dependent on the sulfur content of the product gas. Gas treatment processes can effectively remove up to 99.9% of the sulfur in the feedstock to give a typical product gas having a sulfur concentration of about five parts per million (see Appendix B for a discussion of gas treatment

processes). The sulfur content of the fuel gas is based on the efficiency of the H_2S removal unit in a typical partial oxidation process.

The NO_x emissions are dependent on boiler design and firing characteristics for low-Btu fuel gases produced using air as an oxidant. The nitrogen content of a typical product gas from gasification processes using air oxidation approaches 70% by volume on a dry basis. However, 0.2% nitrogen is typical for gasification processes using oxygen (see Table 2-7). When oxygen is used for oxidation, the product gas is more costly per Btu; but, the potential for NO_x emissions may be greatly reduced due to the low fuel nitrogen content. In theory, the total NO_x emissions could be minimized by eliminating the nitrogen from the partial oxidation process and subsequent combustion. This route is not considered to be economically attractive at the present time.

Particulate emissions from the combustion of fuel gas are directly related to the carbon soot present in the product gas. The carbon soot may be removed from the product gas quite effectively by using water scrubber techniques. The particulate emissions from the combustion of fuel gases from heavy feedstocks are estimated to be below 0.1 pound per million Btu's. NO_x emissions are estimated to be below 0.2 pound per million Btu's using air oxidation, and sulfur oxide concentrations in the flue gas may be less than five parts per million. (36)

Nitrogen oxide emissions in gasification processes cannot be predicted with any degree of certainty at this time, except to say that NO_x emissions should be lower than with conventional systems due to the lower temperatures involved in the combustion. The estimated emission reductions presented here are based on the operation of conventional gasification processes producing a wide variety of product gases.

Impact on the Boiler

It should be feasible to burn cleaned, low-sulfur fuel gas in existing gas-fired boilers. However, because of the low heating value of this gas, some

derating of the boiler may result, as discussed under Applicability.

Converting an existing oil-fired industrial boiler to a low-Btu fuel gas may require a major redesign of the system. In a new installation, the boiler design would consider the heating value of the fuel gas.

For small industrial boilers, it does not appear economically feasible to utilize fuel gas from partial oxidation processes. The cost of processing equipment and related controls for the integration of low-sulfur fuel gas in an industrial boiler could not be justified.

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SECTION 3

CANDIDATES FOR BEST SYSTEMS OF EMISSION REDUCTION FOR CLEAN OIL TECHNOLOGY

3.0 INTRODUCTION

In Section II, we examined three methods of emission control which are applicable to oil-fired industrial boilers. The three techniques considered were:

1. Hydrotreating (HDS) in which fuel oil is treated with hydrogen to produce a clean oil suitable for combustion;
2. Partial Oxidation (POX) in which fuel oil is partially oxidized with oxygen or air to produce a gas which is then scrubbed to remove sulfur, thus making it suitable for combustion; and
3. Chemically Active Fluid Bed (CAFB) in which fuel oil is partially oxidized in a fluid bed of limestone to produce a clean gas suitable for combustion.

In this section, we select the best system of emission reduction and recommend guideline control levels of regulatory options to best achieve moderate, stringent, and intermediate levels of control.

3.1 SELECTION CRITERIA

The factors considered in the selection of the best system of emission reduction from those systems discussed in Section II were:

1. Performance
2. Applicability
3. Status of Development
4. Cost Considerations
5. Energy Considerations
6. Environmental Considerations

In the selection process, an effort was made to rate each of the control systems against each of the selection criteria listed above. For each criterion, the best system was designated 1, the next best 2, etc. The lowest overall score for all criteria was adjudged to be the best system. A summary of the rating evaluation is given in Table 3-1.

3.2 BEST SYSTEMS

From the rating matrix developed in Section 3.1, it is concluded that Hydrotreating (HDS) offers the best system of emission reduction for clean oil technology. A discussion of the ratings for the different selection criteria is given below:

- a) Performance - All three systems will yield a fuel that is environmentally acceptable for burning in a boiler. The overriding consideration in selecting HDS as the best system is its negligible or minor impact on boiler performance. Cleaned liquid fuels are directly applicable to existing industrial boilers with little negative impact on boiler performance. The modest reduction (1-3%) of heat content per gallon of cleaned oil will require additional fuel consumption to achieve rated boiler output. However, burning cleaner fuels will lower the severity of operation and maintenance on the boiler.
- b) Applicability - The HDS system is a clear selection for applicability, since the clean oil produced from HDS can be directly utilized in existing boilers with little impact on the boiler physical facilities. The gasification

TABLE 3-1. RATING MATRIX FOR SELECTION OF BEST SYSTEM OF
EMISSION REDUCTION FOR CLEAN OIL TECHNOLOGY

<u>Control System</u>	<u>Selection Criteria</u>						<u>Total</u>
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	
HDS	1	1	1	1	1	1	6
POX	2	2	2	3	2	3	14
CAFB	3	3	3	2	3	2	16

NOTE: Selection Criteria

1. Performance
2. Applicability
3. Status of Development
4. Cost Considerations
5. Energy Considerations
6. Environmental Considerations

processes require the addition of equipment with attendant cost and space impacts. The retrofitting of either gasification process to an existing industrial boiler could, in some cases, be extremely difficult, if not impossible.

- c) Status of Development - Hydrotreating processing has been in commercial existence for more than 20 years, and over 20 hydrotreating processes are actively in use.⁽¹⁾ The current United States refinery desulfurization capacity is more than 1.8 million barrels per day from 86 plants. However, only 19 plants have direct resid or heavy gas oil hydrodesulfurization facilities which provide a total desulfurization capacity of approximately 0.6 million barrels per day.⁽²⁾

Hydrotreating is an extremely versatile process which is used to desulfurize, denitrogenate, and demetallize fuel oils prior to combustion. It can be adapted to a wide variety of feedstocks ranging from low-sulfur crude oils to high-sulfur residual oils. Hydrotreating used in conjunction with blending can produce fuel oils with almost any characteristics desired. Because of its versatility and widespread use, hydrotreating has been selected as the best candidate under the status of development criterion.

Partial oxidation is a commercially-proven process with more than 200 installations worldwide.⁽³⁾ It, too, is a versatile process that has been used with feedstocks ranging from natural gas through naphtha, residual oil, and even coal. Its primary use has been to produce

synthesis gas for the manufacture of methanol or ammonia; however, there is no technical reason that the synthesis gas cannot be used as a boiler or turbine fuel. The process can be designed to use either air or oxygen as the oxidizing medium, and the product gas will have a heating value of 120 Btu/SCF or 300 Btu/SCF dependent upon whether air or oxygen is used.

The Chemically Active Fluid Bed (CAFB) process is an attractive new technology which could become a significant factor over the next few years in both the utility and industrial areas. It, too, is a versatile process which can be used with a wide selection of feedstocks. The commercial performance and reliability of the CAFB process are yet to be determined. Until this reliability is demonstrated, the CAFB concept is not likely to make a significant impact on the boiler-fuel picture. A CAFB demonstration unit has been constructed and is currently undergoing testing at the La Palma station of Central Power and Light Company at San Benito, Texas.⁽⁴⁾

- d) Cost Considerations - The cost of upgrading liquid fuels in a few large refinery complexes is less demanding than individual emission control techniques at each industrial boiler. In the first place is the matter of mere numbers, wherein we are comparing the cost of desulfurization facilities at less than 100 refineries against individual emission control systems at literally thousands of industrial boiler installations. In addition, the economics of scale would greatly favor the installation of large central

hydrotreating units at refineries rather than smaller installations at individual boilers. For example, a 150×10^6 Btu/hr. oil-fired boiler requires approximately 25 barrels/hr. of oil or 600 barrels per day. A typical 50,000 BPD HDS unit could supply nearly 85 such boilers. Preliminary cost figures show that typical hydrotreating facilities can be installed for investments ranging from \$500 per barrel per stream day capacity for moderate levels of emission control up to \$1,600 per barrel per stream day capacity for the most stringent levels of control.⁽⁵⁾ The costs of producing such cleaned fuels range from \$0.91 to as much as \$5.84 per barrel. The cost of partial oxidation units ranges from \$3,000 to \$6,000 per barrel per stream day with operating costs ranging from \$1.50 to \$7.00 per barrel.⁽⁶⁾ Cost information on CAFB units is very sketchy, but preliminary figures indicate an investment cost of \$3,500-\$4,500 per barrel per stream day and an operating cost of about \$4.00 per barrel.

- e) Energy Considerations - The selection of hydrotreating under this criterion closely parallels the reasoning used for the cost considerations in that the selection is largely determined by numbers and sizes of units. The energy impacts are reflected by the operating cost figures given in the previous paragraph, which indicate that hydrotreating has advantages over both partial oxidation and chemically active fluid bed processing.
- f) Environmental Considerations - There is little difference between the three control systems from an environmental viewpoint. From a practical viewpoint, it is more

advantageous to burn cleaned liquid fuels in industrial boilers rather than handle the environmental problems of untreated fuel oil at each industrial site. The control of potentially-hazardous pollutants can be more effectively managed at the refinery, and the emissions from combustion at industrial boilers can then be more effectively controlled by monitoring the fuel quality.

3.3 REGULATORY OPTIONS

Three regulatory options, which represent moderate, intermediate, and stringent levels of control for SO_2 , NO_x , and particulate emissions, have been selected. The selected emission levels were derived from actual emission data from industrial boilers. Figure 3-1 shows the relationship of sulfur content of the fuel with sulfur oxides emissions; Figure 3-2 shows a similar relationship for NO_x emissions versus nitrogen content of the fuel; Figure 3-3 shows the effect of carbon residue content of the fuel on the particulate emissions.

Table 3-2 gives the maximum sulfur, nitrogen, and carbon residue content of cleaned fuel oil to meet the recommended control levels. The suggested regulatory options are based upon commercially-available systems for the production of low-sulfur fuels from high-sulfur feedstocks. The selected levels of control are based upon the use of residual fuel oil and represent the degree of desulfurization that can be attained using typical refinery processes and technology. Table 3-3 gives the commercially-available hydrodesulfurization technology and illustrates the degree of desulfurization that can be attained with the various processes, feedstocks, and treating conditions.

For the moderate level of control, a suggested fuel content of 0.8% sulfur, 0.3% nitrogen, and 12% carbon residue represents a residual fuel oil that is readily achievable from a number of refinery practices. For the stringent

FIGURE 3-1
EFFECT OF FUEL SULFUR CONTENT ON SO₂ EMISSIONS

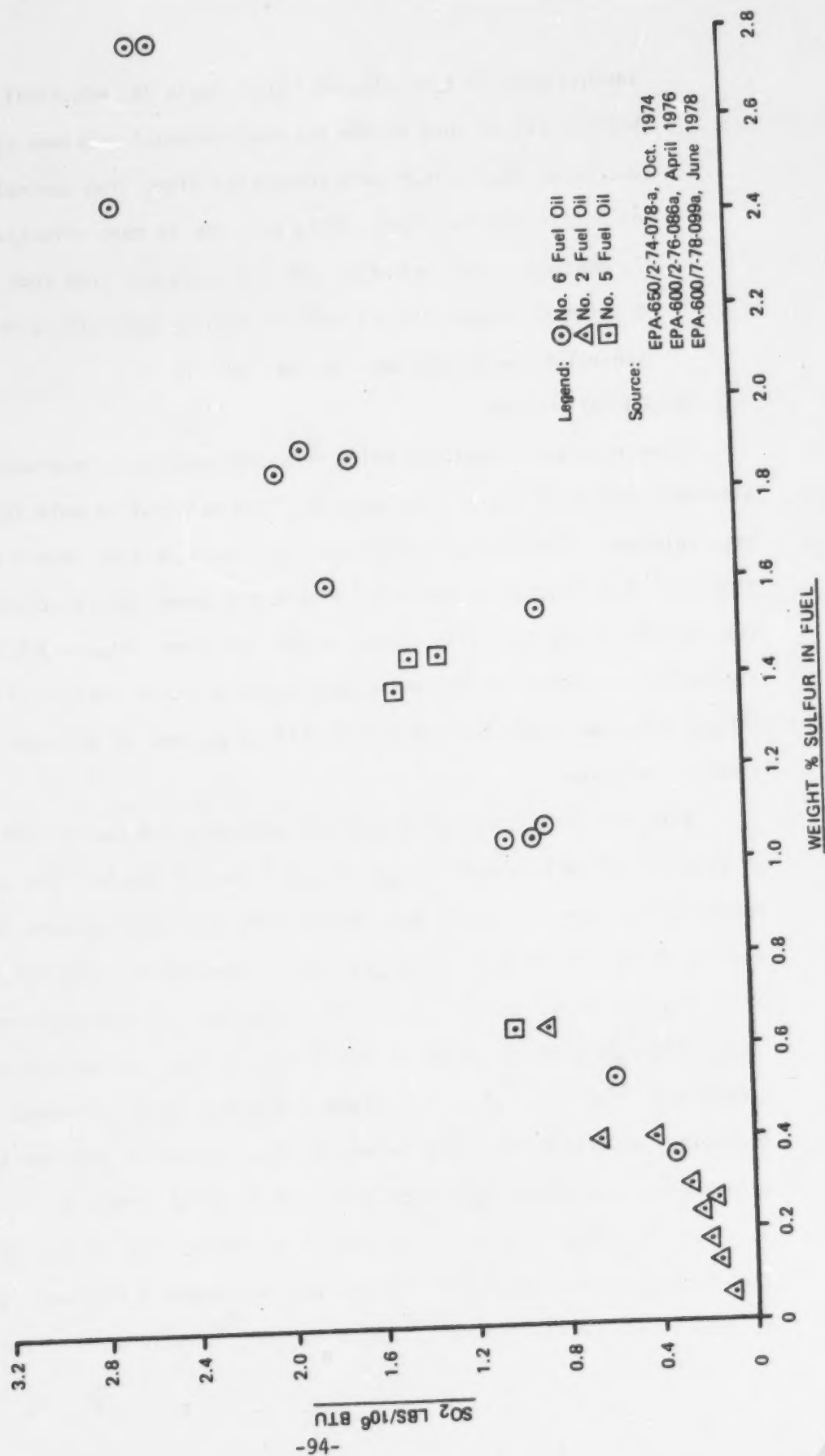


FIGURE 3-2
EFFECT OF FUEL NITROGEN CONTENT ON TOTAL NITROGEN OXIDES

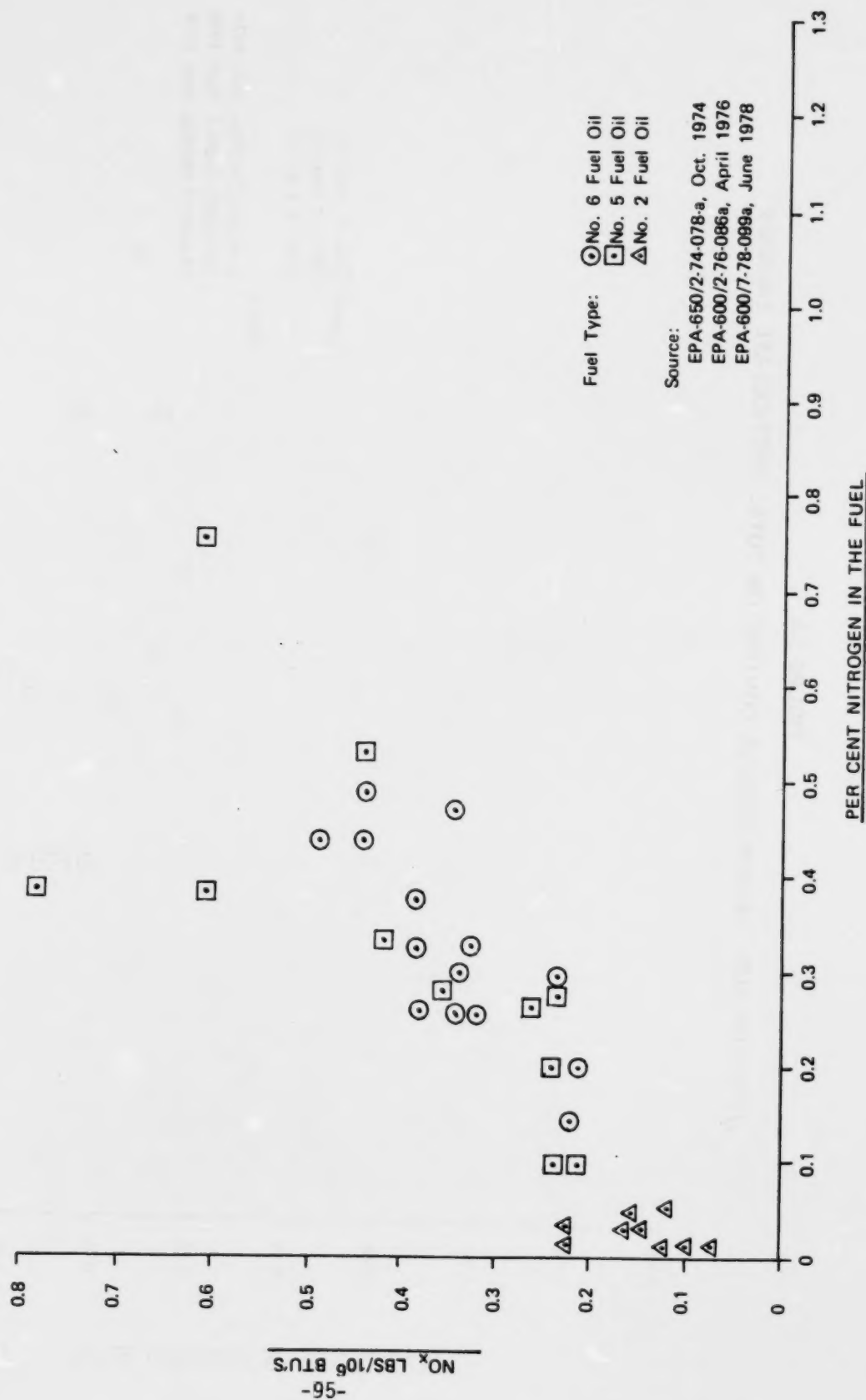


FIGURE 3-3

EFFECT OF FUEL CARBON RESIDUE CONTENT ON TOTAL PARTICULATE EMISSION

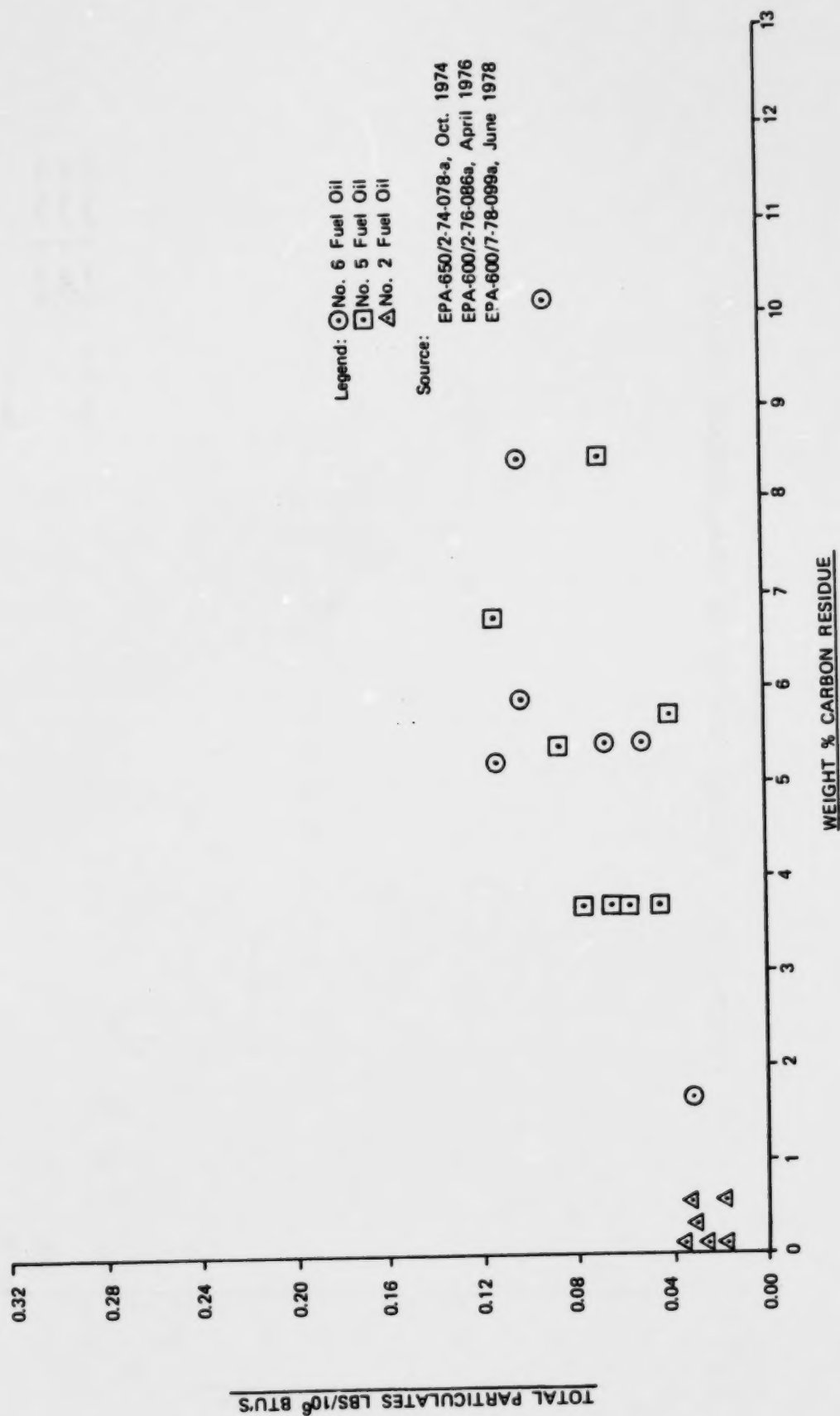


TABLE 3-2. SUGGESTED POLLUTANT CONTENT OF CLEANED FUEL OIL
TO MEET RECOMMENDED CONTROL LEVELS

Pollutant	Control Level					
	Stringent		Intermediate		Moderate	
	Emission #/10 ⁶ Btu	Max. Fuel Content	Emission #/10 ⁶ Btu	Max. Fuel Content	Emission #/10 ⁶ Btu	Max. Fuel Content
SO ₂	0.1	0.1% S	0.3	0.3% S	0.8	0.8% S
NO _x	0.2	0.15% N	0.22	0.2% N	0.3	0.3% N
Particulates	0.05	3.0% C.R.*	0.1	6.0% C.R.	0.25	12% C.R.

* Note: % C.R. = weight percent carbon residue in fuel oil

TABLE 3-3. COMMERCIAL HYDRODESULFURIZATION TECHNOLOGY*

Final Sulfur Level (Wt. %)	Initial S (Wt. %)	% Desulf.	V + Ni ppm (Wt.)	H ₂ Consumption (SCF/BBL)	Feedstock		Process
					Source	Type	
0.1	3.9	97	NR	975	Athabasca	Tar Sands	GO-Fining
	3.8	97	60	960	Kuwait	AR	Gulf IV
	3.8	97	60	700	Kuwait	ATB	Gulf III
	2.9	96	117	410	Arab Heavy	Crude	GO-Fining
	0.46	87	5	NR	S. Louisiana	AR	Gulf II
0.2	3.9	95	60	580	Kuwait	AR	H-Oil
	3.0	93	0	450	Kuwait	VGO	H-Oil
	2.8	93	35	NR	Qatar	AR	Shell
	2.5	90	0	232	Kuwait	VGO	IFP
	2.3	90	40	220	Arab Light	AR	GO-Fining
0.3	1.9	90	220	220	Gach Saran	AR	GO-Fining
	4.2	93	120	915	Arab Heavy	ATB	RESIDfining
	3.8	92	66	770	Kuwait	AR	Gulf III
	3.8	92	46	730	Kuwait	AR	Unicracking
	3.0	90	40	720	Mid East "A"	AR	Gulf III
	3.5	92	60	706	Kuwait	AR	RCD Unibon
	2.1	86	392	NR	Ceuta	Crude	Gulf IV
	3.8	92	60	640	Kuwait	ATB	Gulf III
	2.5	88	220	625	Gach Saran	ATB	RESIDfining
	2.5	88	210	625	Iran Heavy	ATB	RESIDfining
	2.9	90	37	592	Arab Light	AR	Nippon
	2.4	88	220	570	Gach Saran	AR	Union
	3.0	90	40	535	Arab Light	AR	Gulf III
	3.0	90	40	530	Arab Light	AR	Union
	3.8	88	110	480	Iran Light	AR	Gulf IV
	1.6	82	44	340	N. Slope	AR	Union
	2.9	90	105	300	Khafji	AR	GO-Fining
	3.0	90	66	280	Kuwait	AR	GO-Fining
	2.6	87	123	NR	Iran Heavy	AR	Shell
	2.2	85	21	NR	W. Texas	AR	Gulf II
	1.8	84	30	NR	Oman	AR	Shell

* See key at end of table.

TABLE 3-3. COMMERCIAL HYDRODESULFURIZATION TECHNOLOGY* (Cont'd.)

Final Sulfur Level (Wt. %)	Initial S (Wt. %)	% Desulf.	V + Ni ppm (Wt.)	H ₂ Consumption (SCF/BBL)	Feedstock		Process
					Source	Type	
0.4	4.1	89	63	760	Kuwait	AR	IFP
	4.0	90	64	690	Kuwait	AR	LC Fining
	2.7	86	179	NR	Iran Heavy	AR	Shell
	3.2	86	38	560	Arab Light	AR	RDS
	2.6	85	18	NR	Qatar	AR	Shell
0.5	4.4	89	118	950	Khafji	AR	Gulf III
	4.2	88	50	864	Mid East	AR	Shell
	4.2	88	114	825	Mid East "D"	AR	Gulf III
	4.2	88	66	NR	Kuwait	AR	Shell
	3.8	87	60	815	Kuwait	AR	Gulf III
	4.0	88	105	700	Khafji	AR	RESIDfining
	3.8	87	66	660	Kuwait	AR	Gulf III
	3.8	86	55	640	Kuwait	AR	RESIDfining
	3.0	83	40	530	Arab Light	AR	RESIDfining
	2.4	79	210	480	Gach Saran	AR	RESIDfining
	1.8	72	120	295	U. S. Domestic	AR	Gulf II
0.6	4.2	85	66	NR	Kuwait	AR	Shell
	4.2	85	66	NR	Kuwait	AR	Shell
	4.2	85	66	NR	Kuwait	AR	Shell
	3.9	85	115	750	Arab Heavy	AR	RDS
	3.0	80	40	490	Mid East "A"	AR	Gulf II
0.7	2.5	74	183	440	Iranian	AR	Gulf II
	4.6	85	116	965	Mid East "E"	AR	Gulf III
0.8	3.8	80	274	1125	Agha Jari	VR	Gulf II
	4.1	82	101	1000	Arab Light	VR	Gulf II
	4.2	76	114	655	Mid East "B"	AR	Gulf II
	4.3	81	115	NR	Arab Heavy	AR	Shell
0.9	3.5	75	413	1400	Gach Saran	VT	LC-Fining
	5.7	84	163	1250	Kuwait	VTB + VGO	Gulf II
	5.7	85	199	1250	Kuwait	VR	Gulf II

* See key at end of table.

TABLE 3-3. COMMERCIAL HYDRODESULFURIZATION TECHNOLOGY* (Cont'd.)

Final Sulfur Level (Wt. %)	Initial S (Wt. %)	% Desulf.	V + Ni ppm (Wt.)	H ₂ Consumption (SCF/BBL)	Feedstock		Process
					Source	Type	
1.0	4.9	80	NR	1400	Athabasca	Bitumen	H-011
	3.5	71	413	1220	Gach Saran	VTB	H-011
	5.2	79	130	NR	Kuwait	VR	Shell
	5.1	80	115	960	Arab Heavy	VR	VRDS
	4.1	76	38	780	Arab Light	VR	VRDS
	4.4	77	118	685	Khafji	VR	Gulf II
	3.8	74	60	630	Kuwait	AR	Gulf II
	3.8	74	66	515	Kuwait	AR	Gulf II
	3.8	74	60	490	Kuwait	ATB	Gulf II
	3.8	74	75	480	Kuwait	AR	H 011
	2.9	75	195	1410	Arab Heavy	VTB	LC-Fining
1.2	4.0	65	64	520	Kuwait	AR	LC-Fining
1.4	5.8	74	110	820	Mid East "C"	AR	Gulf II

SOURCES: 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15

KEY TO TABLE 3-3

Data

NR = Not Reported

$$\% \text{ Desulf.} = \frac{\text{Initial S} - \text{Final S}}{\text{Initial S}} \times 100$$

Feedstocks

AR = Atmospheric Residuum
 ATB = Atmospheric Tower Bottoms
 VGO = Vacuum Gas Oil
 VR = Vacuum Residuum
 VTB = Vacuum Tower Bottoms

Licensors

Exxon
 Gulf
 Gulf
 Gulf
 Hydrocarbon Research
 Institut Francais du Petrole
 Cities Service/C. E-Lummus
 Nippon Oil
 UOP
 Chevron
 Exxon
 Shell International
 Union Oil
 Chevron

Process Tradename

GO-Fining
 Gulf II HDS
 Gulf III HDS
 Gulf IV HDS
 H-Oil
 HDS
 LC-Fining
 HDS
 RCD/Unibon
 RDS Hydrotreating
 RESIDfining
 Residual Oil Hydrodesulfurization
 Unicracking/HDS
 VRDS Hydrotreating

level of control, a suggested fuel content of 0.1% sulfur, 0.2% nitrogen, and 3% carbon residue represents the highest technically achievable residual fuel oil that can be attained with current technology. It is evident from Figures 3-1, 3-2, and 3-3 that more stringent levels of control can be achieved from the direct use of distillate fuel oils; however, the supply of distillate oils is limited. Therefore, it is necessary to establish recommended control levels that can be achieved with hydrotreated or cleaned residual fuel oils.

Nearly all processes for producing low-sulfur fuels oils rely on the vaporization of distillate, gas oil, or cycle stock materials that can be hydrodesulfurized (HDS) to very low sulfur contents. These desulfurized oils can then be blended with high-sulfur residual oils to produce fuel oils of moderate sulfur content.⁽⁵⁾

There are numerous process variations for producing moderate sulfur content fuel oils, the selection of which is dependent upon the quality of the crude, the amount of upgrading required, and the fuel balance at the refinery. Nearly 95 percent of the low-sulfur fuel oil produced in the U. S. is from one of the following methods or combination of methods: crude distillation, indirect desulfurization of vacuum gas oil, or desulfurization of feedstock from catalytic cracking, delayed, or fluid coking.

The lowest cost production method is the straight distillation of low-sulfur crudes. Some crudes are low enough in sulfur that simple crude distillation not only yields distillates and gas oils low in sulfur but even the 700°F+ topped crudes may contain less than 0.4% sulfur. These low-sulfur products can be blended with higher-sulfur products from other refinery processes, thus avoiding any direct hydrodesulfurization processing.

Another method, called indirect desulfurization, is used as a moderate reduction control method. This method involves flashing of topped crude under vacuum and hydrodesulfurization of the vacuum gas oil (VGO). Up to 95 percent of the sulfur in the vacuum gas oil can be removed by hydrodesulfurization,

yielding a desulfurized oil containing from 0.1 to 0.3 percent sulfur. These desulfurized oils can be blended with residual oils to give moderate control level fuels.

Increasingly-stringent restrictions on sulfur emissions have reduced the available markets for high-sulfur fuel oils and have forced the refinery industry into more and more bottoms processing. One such process is residuum desulfurization, which is used to produce low-sulfur fuel oils directly from atmospheric distillation bottoms. The level of desulfurization required for intermediate reduction control is removal of about 80% of the sulfur from the atmospheric residua, which may contain 3.5 percent, or more, of sulfur. Higher levels of desulfurization can be achieved but only at greatly-increased costs. Additional processing steps are needed for handling atmospheric bottoms rather than vacuum gas oil. For example, feed filters are required to remove various contaminants such as dirt and carbon usually found in residual oils. In addition, guard reactors are required to remove metals such as nickel and vanadium which would otherwise rapidly deactivate the expensive hydrodesulfurization catalysts.

The crude type also has a significant effect on the processing cost from atmospheric residuum. The properties of atmospheric residua derived from typical crudes may vary widely in sulfur content, metals, and carbon. Two major processing expenses are the cost of hydrogen, which is a function of the sulfur and nitrogen content of the feed, and the cost of catalyst, which is a function of the metals content of the feed. The hydrogen- and catalyst-related costs typically represent 65-75% of the total processing cost of making low-sulfur fuel oil from atmospheric bottoms.⁽¹⁸⁾

The crude type also has a significant effect on the desulfurization efficiency of a processing unit. Table 3-4 illustrates how the performance of a unit designed to reduce Kuwait atmospheric residuum to a 0.3% sulfur product is rated for three other resids.⁽¹⁹⁾

TABLE 3-4. EFFECT OF CRUDE SWITCHES ON HDS UNIT CAPABILITY

<u>Crude</u>	<u>650°F+ Atmospheric Bottoms</u>			<u>Product* Sulfur Wt. %</u>
	<u>Sulfur, Wt. %</u>	<u>Metals, ppm</u>	<u>Gravity, °API</u>	
Kuwait (design)	4.11	60	14.8	0.30
Light Arabian	2.99	30	17.7	0.19
Heavy Iranian	2.50	221	15.0	0.29
Heavy Arabian	4.19	120	12.3	0.43

* 11 months - cycle length at constant operating conditions

Source: Edelman, A. M., et al, "A Flexible Approach to Fuel Oil Desulfurization," Japanese Petroleum Institute Meeting, 8 May 1975(19)

For the stringent level of control, very rigorous hydrodesulfurization of atmospheric residuum is necessary. To achieve this high level of desulfurization with high product yields, an average desulfurization efficiency of 97% is required. To reduce the sulfur content of high-sulfur residuals to 0.1% by weight requires two or more stages of hydrodesulfurization or one stage of hydrodesulfurization coupled with other conversion processes such as fluid coking or demetallization. These techniques for producing 0.1% sulfur fuel oil from high sulfur resids have been in commercial operation for approximately 3-5 years.

3.4 SUMMARY

Table 3-5 summarizes the characteristics of typical hydrodesulfurization processes by level of sulfur content reduction. As shown in the table, the average capital investment, as well as the overall energy requirements, increase with increasing degree of desulfurization.

Hydrotreating processes which produce cleaned liquid fuels are considered the best system of emission reduction applicable to oil-fired industrial boilers. The processes which clean oil by gasification are either not generally suited to the small scale of industrial boilers (POX) or are not commercially demonstrated (CAFB).

Guideline control levels or regulatory options to best achieve moderate, stringent, and intermediate levels of control are selected.

Hydrotreating processes are considered the best emission control techniques for all three levels of control.

TABLE 3-5. CHARACTERISTICS OF TYPICAL HYDRODESULFURIZATION
PROCESSES BY LEVEL OF REDUCTION IN SULFUR CONTENT*

<u>Factor</u>	<u>Control Levels</u>		
	<u>Moderate</u>	<u>Intermediate</u>	<u>Stringent</u>
Investment, \$ per bpsd capacity	680-1150	1080-1410	1360-1620
Utilities, units/bbl. feed			
fuel fired, MBTU	82-90	92-95	94-96
power, kwh	5.7-8.0	7.2-9.7	7.6-9.9
cooling water, gal.	120-140	140-150	150-160
steam, MBTU	28-49	44-80	49-84
Wt. % Sulfur in product	0.8	0.3	0.1

* Basis - Range of values for five residual oils encompassing low- to high-sulfur contents (2.1-4.6%) and low to high metals (60-292ppm). Details are discussed in Section 4.

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SECTION 4

ECONOMIC IMPACT OF BEST EMISSION CONTROL SYSTEM

4.0 INTRODUCTION

In Section 3, we selected hydrodesulfurization (HDS) as the best system of emission reduction for clean oil technology and recommended guideline control levels of regulatory options to best achieve moderate (0.8%S), intermediate (0.3%S), and stringent (0.1%S) levels of control.

In this section, we determine the cost of hydrodesulfurization to produce cleaned fuel oils to meet the required control limits and assess the economic impact of burning desulfurized oils in industrial boilers.

In our cost analyses, only direct desulfurization of residual fuel oil is considered. Indirect desulfurization, or the procedure of desulfurizing a light distillate and back blending with residua to produce the required product level, is not capable of achieving the intermediate and stringent levels of control and therefore is not considered in this study.

The cost of hydrodesulfurization of residual fuel oil is a function not only of the sulfur content but also of the crude source from whence the residual was derived and of the metal content of the residual. Since there are literally hundreds of different crude oils and, consequently, a like number of residua, it is virtually impossible to select a typical residual oil that would be representative of all these crudes. Accordingly, we have selected a group of five residual oils which cover a range of sulfur and metal values and which will accommodate virtually all the known crudes within the limits covered by these five residua. The five residua considered in this section can be classified as follows:

<u>Residua</u>	<u>Classification</u>
1. Ceuta	Low sulfur, high metals
2. E. Venezuelan	Low sulfur, high metals
3. Kuwait	Medium sulfur, low metals
4. Khafji	High sulfur, moderate metals
5. Cold Lake	High sulfur, high metals

The cost of hydrodesulfurization is also highly dependent upon the degree of desulfurization. In order to cover as wide a range as possible, the hydrodesulfurization costs were calculated for the three recommended levels of control, as well as the State Implementation Plan (S.I.P) level of 1.6% sulfur currently being used in most of the United States.

4.1 SUMMARY

A summary of the hydrodesulfurization costs for the five residual fuel oils and four levels of sulfur content is given in Table 4-1.

TABLE 4-1. SUMMARY COSTS OF HYDRODESULFURIZATION OF RESIDUAL FUEL OIL

<u>Residual Fuel Oil</u>		<u>Percent Sulfur in Treated Oil</u>				
<u>Type</u>	<u>% Sulfur</u>	<u>ppm (Ni + V)</u>	<u>1.6 \$/B</u>	<u>0.8 \$/B</u>	<u>0.3 \$/B</u>	<u>0.1 \$/B</u>
Ceuta	2.12	292	0.91	2.28	3.91	5.28
E. Venezuelan	2.38	274	1.17	2.45	3.93	5.71
Kuwait	3.80	60	1.80	2.49	3.14	3.51
Khafji	4.36	118	2.20	2.85	3.60	4.11
Cold Lake	4.55	236	2.52	3.42	4.53	5.84

As evidenced from the foregoing table, the cost of HDS ranges from a low of \$0.91 per barrel for the hydrodesulfurization of a low-sulfur, high metals residua to a high of \$5.84 per barrel for the hydrodesulfurization of a high-sulfur, high metals residua.

It is also evident that the cost of HDS escalates quite rapidly with the degree of desulfurization, going from \$0.91/B for the desulfurization of Ceuta residual to a level of 1.6% sulfur to a cost of \$5.28/B for desulfurizing to a level of 0.1% sulfur. This represents a cost of \$14.46/bbl for the 1.5% S Ceuta oil, or 39% over the cost of untreated oil.

The foregoing table also indicates that the cost of desulfurization to the S.I.P. (1.6%S) and moderate (0.8%S) levels is primarily a function of the sulfur level of the untreated oil; whereas, desulfurizing to the intermediate (0.3%S) and stringent (0.1%) levels clearly reflects the influence of metals content on desulfurization cost. It further shows that, regardless of the type of residual feed, the cost of desulfurizing to very low levels such as 0.1%S is substantial, ranging from \$3.51 to \$5.84 per barrel or 26 to 43 percent more than the cost of untreated oil. This effect is more clearly shown in Figure 4-1, which shows the cost of high, low, and medium sulfur content residuals versus the sulfur level of the desulfurized oil. By way of comparison, Figure 4-2 gives the prices of residual fuel oil as quoted in the Oil and Gas Journal, and it can be seen that these agree reasonably well with the cost curves derived from this study.

Table 4-2 is a further summary of the data shown in Figure 4-1 and gives a cost breakdown into the principal cost elements. This table vividly illustrates the effect of hydrogen and catalyst costs on the overall cost of desulfurization which range from 33 to 61% of the total cost. The effect of these and the other cost elements is further discussed in later sections of this report.

Table 4-3 gives the cost impact of low sulfur fuel oil firing in industrial boilers. Data are presented for small (4.4MW, 15,000 MBtu/Hr.) commercial-type boilers and for large (44MW, 150,000 MBtu/Hr.) industrial-type boilers. These sizes represent typical maximums for these type boilers. It is assumed that the small boilers are fired with distillate oil (No. 2),

Figure 4-1
COST OF DESULFURIZED RESIDUAL FUEL OIL

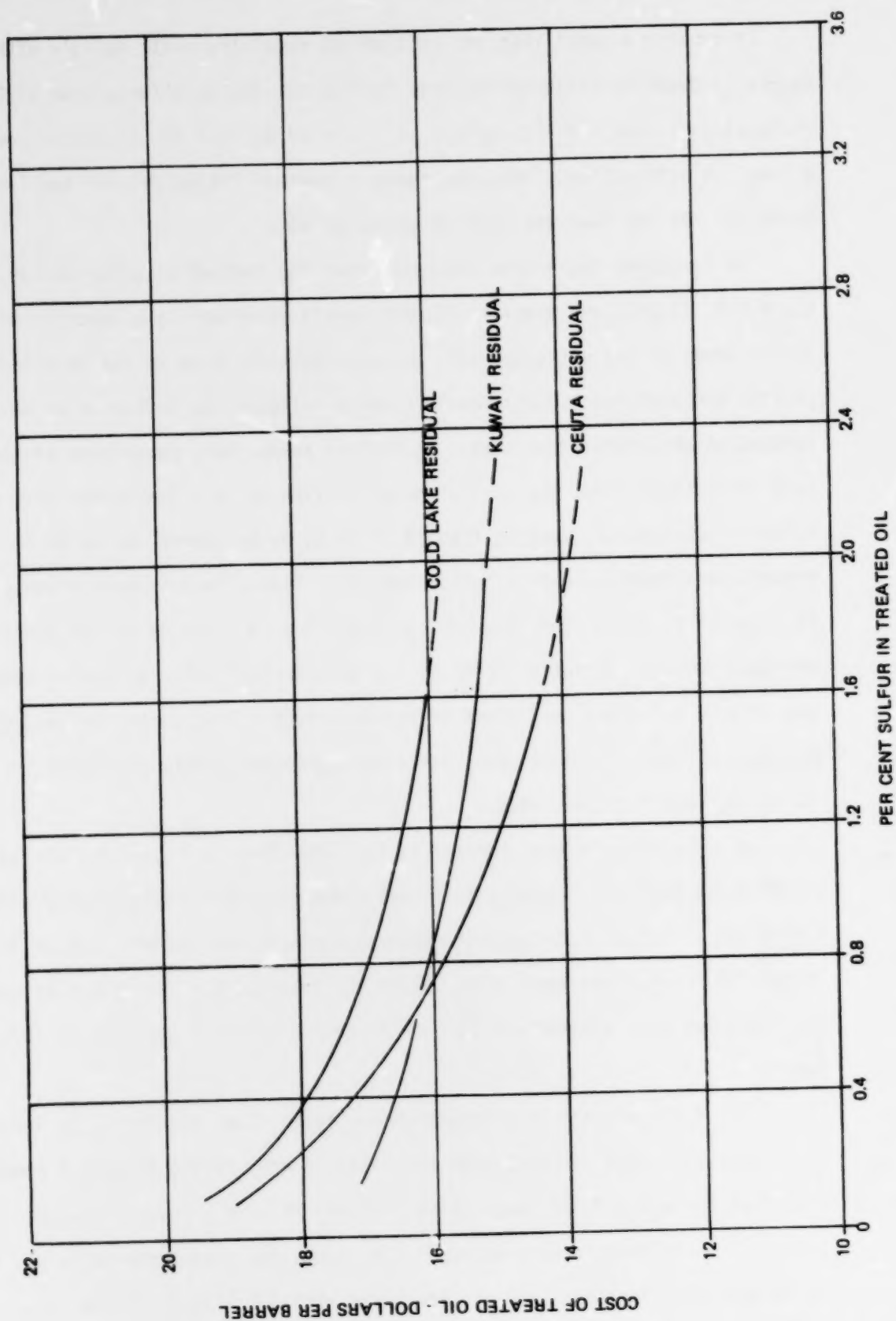


Figure 4-2

COST OF RESIDUAL FUEL OIL (NO. 6)
OF VARIOUS SULFUR CONTENT

Source - Oil and Gas Journal May 29, 1979

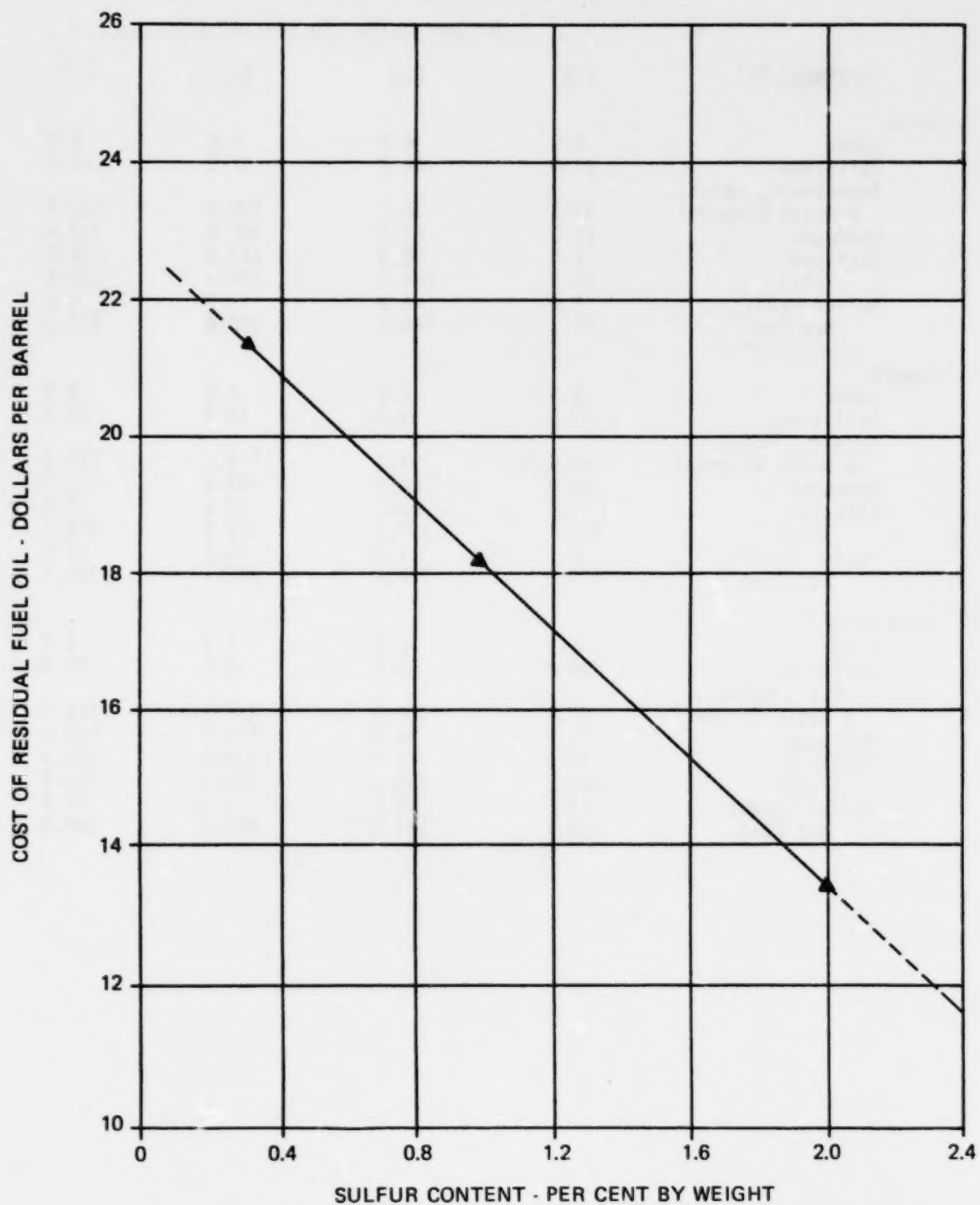


TABLE 4-2. COST DISTRIBUTION FOR THREE RESIDUA (¢/bbl)

<u>Residual Oil</u>	<u>Percent Sulfur in Treated Oil</u>			
	<u>1.6</u>	<u>0.8</u>	<u>0.3</u>	<u>0.1</u>
Ceuta				
Labor	6.9	6.9	6.9	6.9
Utilities	24.9	49.7	62.0	65.7
Investment, Maint., & Waste Disposal	31.5	70.1	105.8	129.6
Hydrogen	21.0	67.0	102.0	117.0
Catalyst	9.0	38.0	121.0	216.0
Total	93.3	231.7	397.7	535.2
Sulfur Credit	2.0	5.0	6.9	7.6
Net Cost	91.3	226.7	390.8	527.6
Kuwait				
Labor	6.9	6.9	6.9	6.9
Utilities	47.8	59.4	73.4	76.9
Invest., Maint., & Waste Disposal	64.4	91.1	119.6	141.8
Hydrogen	58.0	88.0	107.0	115.0
Catalyst	11.0	15.0	20.0	24.0
Total	188.1	260.4	326.9	364.6
Sulfur Credit	8.3	11.3	13.2	13.9
Net Cost	179.8	249.1	313.7	350.7
Cold Lake				
Labor	6.9	6.9	6.9	6.9
Utilities	54.2	64.8	80.4	82.9
Invest., Maint., & Waste Disposal	97.1	116.0	139.5	156.9
Hydrogen	70.0	96.0	113.0	120.0
Catalyst	35.0	72.0	129.0	234.0
Total	263.2	355.7	468.8	600.7
Sulfur Credit	11.1	14.1	16.0	16.7
Net Cost	252.1	341.6	452.8	584.0

whereas the larger industrial boilers are fired with residual oil (No. 6).

From Table 4-3, it is evident that the cost impact of providing low sulfur distillate oil for firing small commercial boilers is minimal, amounting to just a 6.7% premium for 0.3% S and 7.7% premium for 0.1% S oil. This small effect is primarily brought about as a result of the small amount of desulfurization required to desulfurize regular No. 2 distillate oil, which usually contains 0.5% (or less) sulfur, to these lower sulfur levels.

The cost impact of using residual fuel oil is much more dramatic, ranging from a premium of 6.7 to 18.6% when using oil desulfurized to a level of 1.6% S up to a premium of 39 to 43.1% when using oil desulfurized to a level of 0.1% S.

Table 4-4 shows the cost effectiveness of fuel oil desulfurization for the five residua considered, as well as for the distillate fuel oil. Generally, these data indicate that the cost effectiveness improves as the sulfur content of the residuum feed rises, provided that the metal content does not increase as well.

A comparison of the Kuwait and Khafji data shows the effect of similarity between sulfur levels combined with relatively similar metal levels. The Cold Lake data vividly show the strong effect of high metal levels.

The data of Table 4-4 also indicate that, for a given feedstock, fuel oil desulfurization tends to be less cost effective as the degree of desulfurization increases. This effect ranges from 17% to 65%, depending on the specific residuum; but, the trend is quite general.

4.2 PROCESS DESCRIPTIONS

A modern hydrodesulfurization facility designed to meet EPA Clean Air Requirements consists of four basic process elements, namely:

1. Hydrodesulfurization (HDS) Unit
2. Hydrogen (H_2) Plant
3. Sulfur (S) Plant
4. Sulfur Tail Gas Cleaning (SCOT) Plant

TABLE 4-3. COST IMPACT OF LOW SULFUR FUEL OIL FIRING IN BOILERS

System Standard Boilers Heat Input MW (MBTU/HR)	Type	Type & Level of Control	Crude Source	Control Efficiency (%S)	Annual Costs		Cost Impact	
					\$ /kJ/S	\$ /MBTU/ HR	% Over Uncon- trolled	% Over S.I.P. Controlled
44 (150,000)	Watertube	LSFO	Ceuta	S.I.P. Moderate Intermediate Stringent	1.6 0.8 0.3 0.1	4.03 10.03 17.23 23.27	1.18 2.94 5.05 6.82	N/A 6.72 16.82 28.86 39.04
		Low Sulfur Resid ($\leq 3\%$ S)	E. Venezuelan	S.I.P. Moderate Intermediate Stringent	1.6 0.8 0.3 0.1	5.15 10.78 17.30 25.15	1.51 3.16 5.07 7.37	N/A 8.63 18.08 29.00 42.14
		Medium Sulfur Resid (3.8% S)	Kuwait	S.I.P. Moderate Intermediate Stringent	1.6 0.8 0.3 0.1	7.92 10.95 13.82 15.46	2.32 3.21 4.05 4.53	N/A 13.28 18.38 23.17 25.90
		High Sulfur Resid ($> 4\%$ S)	Khafji	S.I.P. Moderate Intermediate Stringent	1.6 0.8 0.3 0.1	9.69 12.56 15.87 18.12	2.84 3.68 4.65 5.31	N/A 16.24 21.03 26.57 30.33
4.4 (15,000)	Firetube	LSFO	Cold Lake	S.I.P. Moderate Intermediate Stringent	1.6 0.8 0.3 0.1	11.09 15.08 19.96 25.73	3.25 4.42 5.85 7.54	N/A 18.60 25.24 33.43 43.10
		Distillate Fuel Oil	N/A	S.I.P. Moderate Intermediate Stringent	0.3 0.1	N/A N/A 5.46 6.21	N/A N/A 1.60 1.82	N/A N/A 6.73 7.67
								N/A N/A N/A 0.88

TABLE 4-4. COST EFFECTIVENESS

Crude Source	Sulfur In Fuel Oil %	Cost/Unit Removal	
		\$/lb	\$/KG
Ceuta	1.6	0.52	1.14
	0.8	0.51	1.13
	0.3	0.64	1.40
	0.1	0.78	1.71
E. Venezuelan	1.6	0.45	0.99
	0.8	0.46	1.01
	0.3	0.56	1.23
	0.1	0.74	1.63
Kuwait	1.6	0.24	0.53
	0.8	0.25	0.55
	0.3	0.27	0.59
	0.1	0.28	0.62
Khafji	1.6	0.24	0.53
	0.8	0.24	0.53
	0.3	0.26	0.57
	0.1	0.29	0.64
Cold Lake	1.6	0.25	0.55
	0.8	0.27	0.59
	0.3	0.32	0.70
	0.1	0.39	0.86
Distillate	0.2	0.20	0.44
	0.1	0.21	0.46

Figure 4-3 shows a typical HDS unit for the desulfurization of residual oil. Residual oil feed is heated together with make-up hydrogen and recycle gas, and the mixture charged to the reactor section. The reactor section consists of one or more reactors in series, with the number being dependent upon the degree of desulfurization required. When treating feeds containing high levels of metals (Ni + V), a guard reactor is used to minimize the contamination of the more valuable catalyst used in the desulfurization reactors. Hydrogen-rich gas is flashed from the reactor effluent in a high-pressure separator and is purified by amine scrubbing prior to recycling to the reactor section. Liquid from the high pressure separator passes through a low-pressure separator to remove H_2S and fuel gas and then goes to the fractionator for separation of naphtha, middle distillate, and low sulfur fuel oil.

Figure 4-4 shows a typical hydrogen plant for the production of hydrogen by the steam reforming of natural gas, LPG, or naphtha. Hydrocarbon feed is first desulfurized to prevent poisoning of the reforming catalyst. The desulfurized feed is mixed with superheated steam and reformed by passing through catalyst-filled tubes in the reformer furnace. The reformed gas containing hydrogen, carbon monoxide, carbon dioxide, and steam is cooled and then passed through a shift converter where the carbon monoxide is reacted with steam to produce carbon dioxide and hydrogen. The CO_2 -rich gas is then scrubbed with amine to remove essentially all the carbon dioxide. The remaining traces of carbon monoxide and carbon dioxide are removed by passing the gas through the methanator, wherein the CO_2 and CO are reacted with hydrogen to form methane. The methanator effluent gas typically contains 95-98% H_2 .

Figure 4-5 shows a typical Claus-type sulfur recovery plant. Hydrogen sulfide gas is fed to a modified fire-tube boiler where it is partially burned with air to form sulfur dioxide. The amount of air is controlled to limit the combustion to one-third of the H_2S fed. Effluent gas from the boiler consisting of $2/3 H_2S$ and $1/3 SO_2$ is passed through a primary converter wherein H_2S

FIGURE 4-3
TYPICAL HDS UNIT

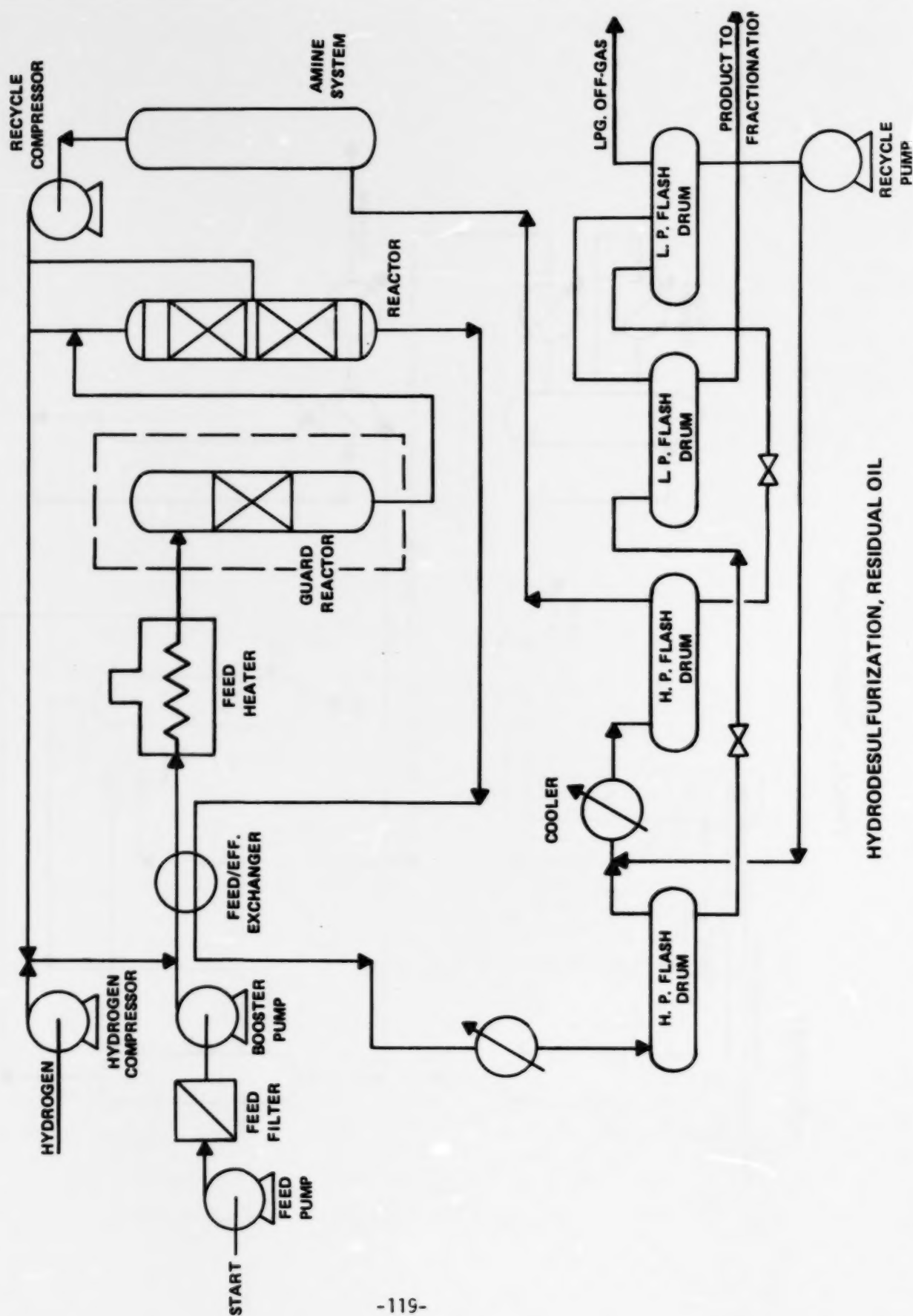


Figure 4-4
TYPICAL HYDROGEN PLANT

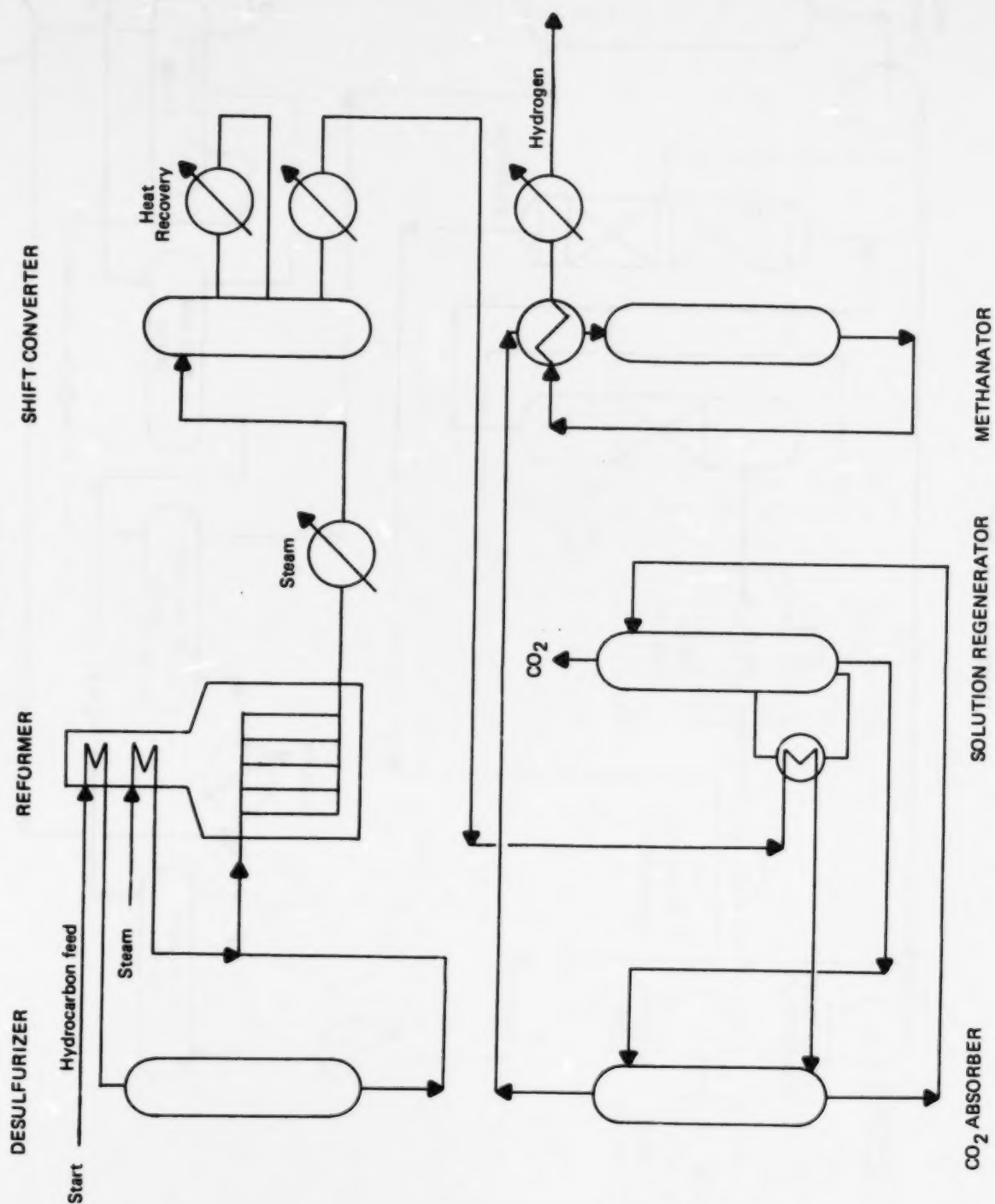
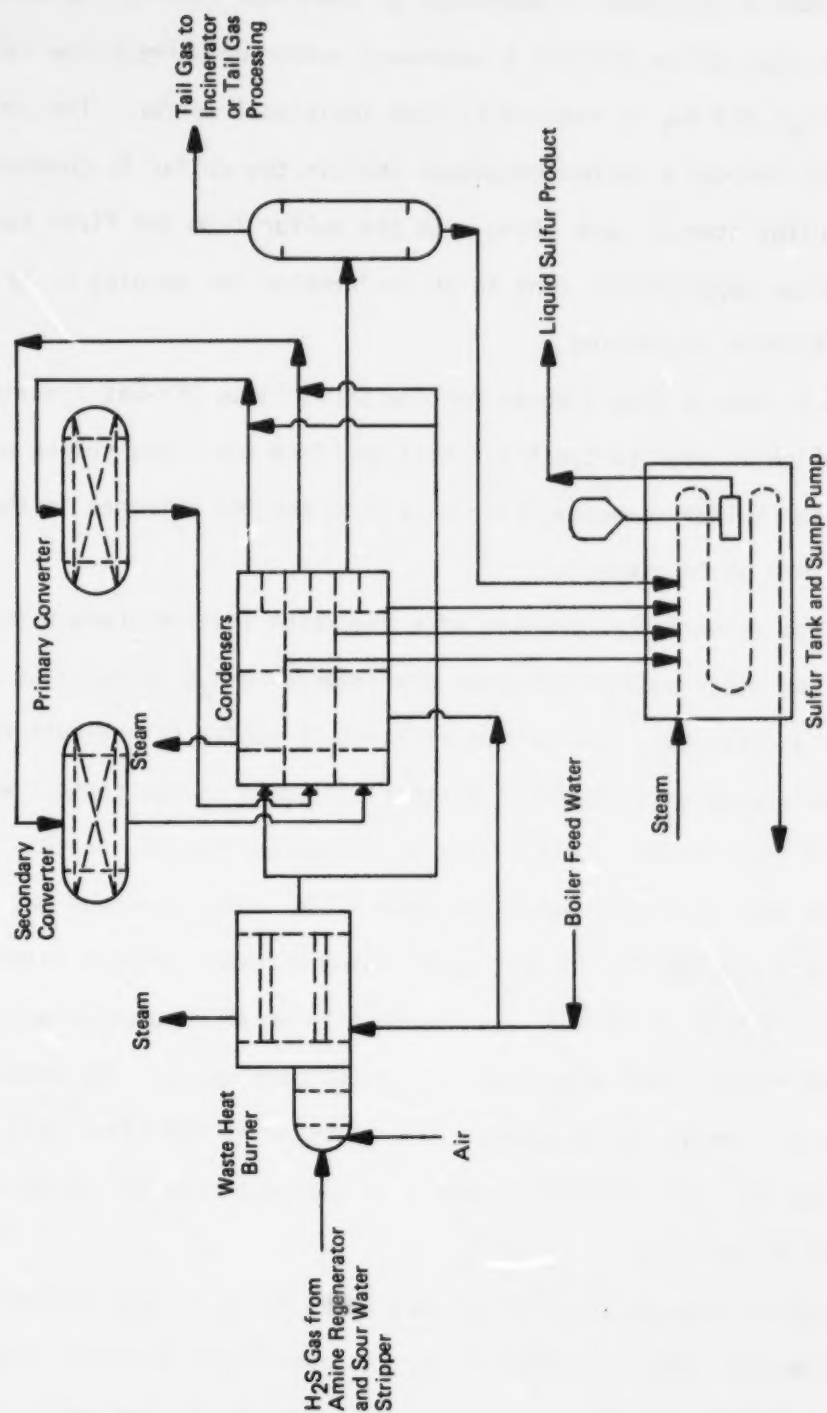


Figure 4-5
TYPICAL PACKAGED CLAUS PLANT (2 STAGE)



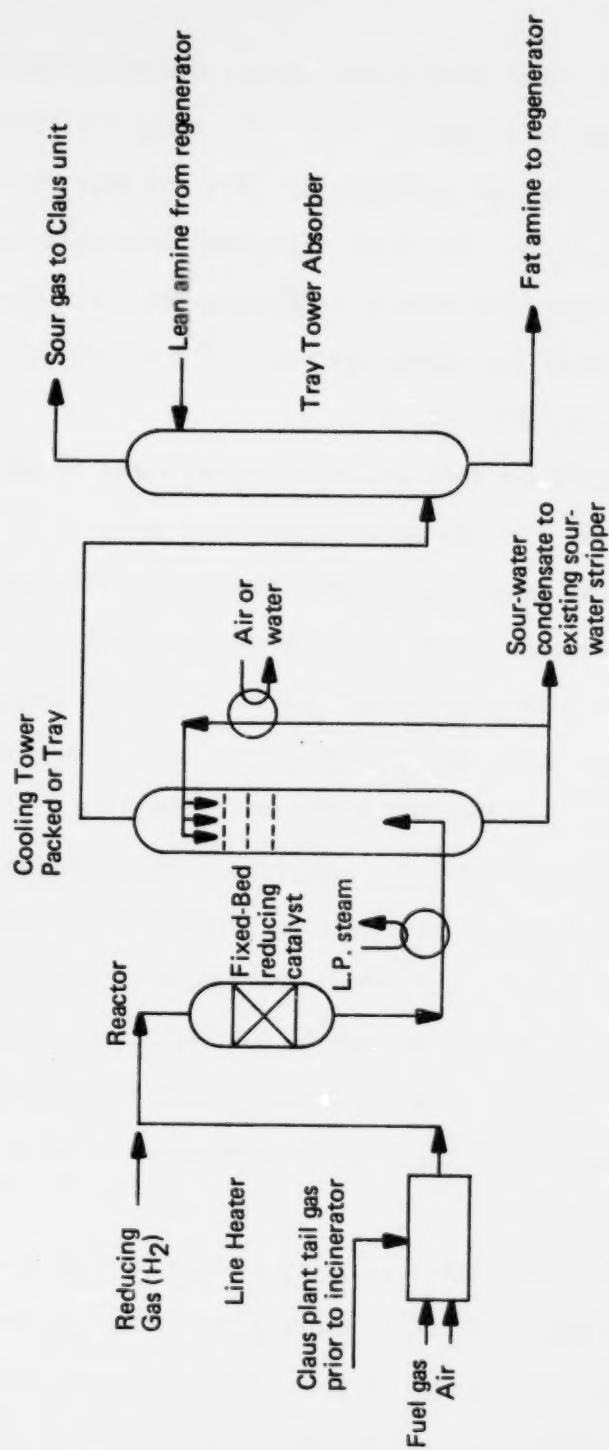
is reacted with SO_2 to form sulfur vapor and steam. The converter effluent passes through a primary condenser wherein the sulfur vapor is condensed out of the gas stream while steam is generated on the other side of the condenser. The gas stream then passes through a secondary converter wherein the bulk of the remaining H_2S and SO_2 is reacted to form additional sulfur. The converter effluent passes through a second condenser wherein the sulfur is condensed and sent to the sulfur storage tank along with the sulfur from the first condenser. Tail gas from the separator is sent to an incinerator for burning or to a Tail Gas Unit for further processing.

Figure 4-6 shows a flow diagram for the Shell Claus Off-Gas Treating Process (SCOT) which is used to treat the tail gas from the Claus sulfur plant and to increase the sulfur recovery efficiency from the 95% obtained in the Claus unit to more than 99.8% overall.

The process essentially consists of a reduction section wherein the SO_2 , free sulfur, and other sulfur compounds are reduced to H_2S by reaction with hydrogen over a catalyst. The reactor effluent is cooled by indirect exchange to produce low pressure steam and is further cooled by direct contact with water in a packed or tray column. Water vapor is condensed from the process gas and the condensate sent to a sour water stripper. The cooled overhead gas containing up to 3% H_2S and 40% CO_2 is sent to an amine absorber wherein essentially all the H_2S and little of the CO_2 are absorbed by an ADIP solution which, depending on conditions, uses a secondary or a tertiary amine. The recovered H_2S is stripped from the amine solution and recycled to the Claus unit whereas the treated gas from the absorption column is vented to the air or is burned in a standard incinerator.

The foregoing process descriptions are meant to be typical rather than specific and do not imply a preference to any proprietary process. There are a number of suppliers for each of the foregoing processes; and, while details of the processes may vary, the overall results for the various processes are

Figure 4-6
Flow Diagram for the Shell Claus Off-Gas (Scot) Treating Process



the same. For that reason, the processes must be considered equivalent.

4.3 COST BASIS

Table 4-5 gives HDS plant details for various hydrodesulfurization processes as reported in the literature.⁽¹⁾⁽²⁾⁽³⁾⁽⁴⁾ Table 4-6 lists selected data from Table 4-5 for the five residual fuel oils and four levels of desulfurization used in this study. The plant investment data shown in Table 4-6 have been updated to a June 1978 base by escalating the costs given in Table 4-5 by multiplying by the factor derived from the Chemical Engineering Plant Cost Index given in Table 4-7.

It is seen from Table 4-5 that the units listed range in capacity from 30,000 B/D to 78,000 B/D, with the majority having a capacity of 50,000 B/D. The size of HDS units may range from several thousand barrels per day to one hundred thousand or more barrels per day; however, the vast majority of new installations will fall within the 25,000 B/D to 75,000 B/D range. The maximum capacity that can be built into a single-train unit is approximately 25-30,000 B/D; hence, we see that HDS plant capacities tend to cluster around 25,000 B/D, 50,000 B/D, and 75,000 B/D capacities - representing one-, two-, and three-train plants, respectively. Due to this limit for single-train capacity, one does not realize much effect on economy of scale in going from 25,000 B/D capacity to 50,000 B/D or even 75,000 B/D. This fact, coupled with the fact that most of the data given in Table 4-5 are for 50,000 B/D capacity, has led us to select 50,000 B/D capacity as representative of current refinery practice.

Table 4-5 further illustrates that single-stage systems are used to reduce sulfur levels to about 0.8% (80% removal), two-stage systems to about 0.3% (90% removal), and three-stage or two-stage with guard reactor to about 0.1%. HDS plant cost versus percent sulfur in the treated oil (or percent removal) is assumed to be a continuous function rather than a step function, as described above, and as illustrated by Figure 4-7, which shows the costs of

TABLE 4-5
HDS PLANT DETAILS
FOR
HYDRODESULFURIZATION OF RESIDUAL FUEL OILS

Licenser	Type	Capacity B/CD	Residuuum Fed	Feed %S	Product %S	Removal %*	Reported Cost MM \$	Year	1978 Cost MM \$
GULF	II	50,000	Cold Lake	4.55	1.14	74.9	43.5	1975	52.2
GULF	II	50,000	Khafji	4.36	1.09	75.0	30.3	1975	36.4
UOP	RCD ISOMAX	40,000	Kuwait	3.8	1.0	73.7	17.1	1972	27.3
GULF	II	30,000	Kuwait	5.5	1.0	81.8	34.7	1975	41.6
	II	50,000	Kuwait	5.5	1.0	81.8	32.7	1974	43.3
	II	50,000	Kuwait	3.8	1.0	73.7	30.6	1975	36.4
	II	50,000	Kuwait	3.8	1.0	73.7	28.8	1974	38.1
	II	50,000	Khafji	4.4	1.0	77.3	34.3	1974	45.4
UOP	RCD Isomax	40,000	Tiajuana	2.61	0.9	65.5	20.1	1972	32.1
GULF	II	50,000	Iranian	2.47	0.62	74.9	34.0	1975	40.8
GULF	II	50,000	E. Venezuela	2.38	0.60	74.8	38.4	1975	46.1
GULF	II	50,000	Ceuta	2.12	0.53	75.0	36.0	1975	43.2
	VGO/NRDS	78,000	Arab Heavy	4.4	0.5	88.6	34.8	1973	52.8
	RDS	78,000	Arab Heavy	4.4	0.5	88.6	38.9	1973	59.1
UOP	RCD ISOMAX	40,000	Kuwait	3.8	0.5	86.8	23.0	1972	36.7
UOP	RCD ISOMAX	40,000	Kuwait	3.8	0.32	91.6	27.7	1972	44.2
GULF	III	50,000	Kuwait	3.8	0.3	92.1	43.5	1975	52.2
	III	50,000	Iranian	2.47	0.3	87.9	43.5	1975	52.2
	III	50,000	Ceuta	2.12	0.3	85.8	44.9	1975	53.9
	III	50,000	E. Venezuela	2.38	0.3	87.4	48.3	1975	58.0
	III	50,000	Khafji	4.36	0.3	93.1	51.3	1975	61.6
	III	50,000	Kuwait	3.8	0.3	92.1	45.6	1974	60.3
	III	50,000	Cold Lake	4.55	0.3	93.4	58.8	1975	70.6
GULF	IV	50,000	Kuwait	3.8	0.1	97.4	56.3	1974	74.5

TABLE 4-6. HDS PLANT INVESTMENT

Based on HDS of 50,000 B/D of Residual Oil Costs Updated to June 1978

<u>Residual Oil</u>		<u>Percent Sulfur in Treated Oil</u>			
		1.6	0.8	0.3	0.1
		Cost in Millions of Dollars			
Ceuta	2.12% S	15.0	34.0	54.0	68.0
Venezuelan	2.38% S	24.0	40.0	58.0	72.0
Kuwait	3.80% S	28.5	42.5	60.0	74.5
Khafji	4.36% S	40.0	48.0	62.0	77.0
Cold Lake	4.55% S	48.5	57.5	70.5	81.0

TABLE 4-7. ECONOMIC INDICATORS

CE PLANT COST INDEX

<u>Year</u>	<u>CE Index</u>	<u>Multiplier to Get 1978 Cost</u>
1970	125.5	1.743
1971	132.2	1.655
1972	137.2	1.595
1973	144.1	1.518
1974	165.4	1.323
1975	182.4	1.200
1976	192.1	1.139
1977	204.1	1.072
1978	218.8	1.000

M & S EQUIPMENT COST INDEX

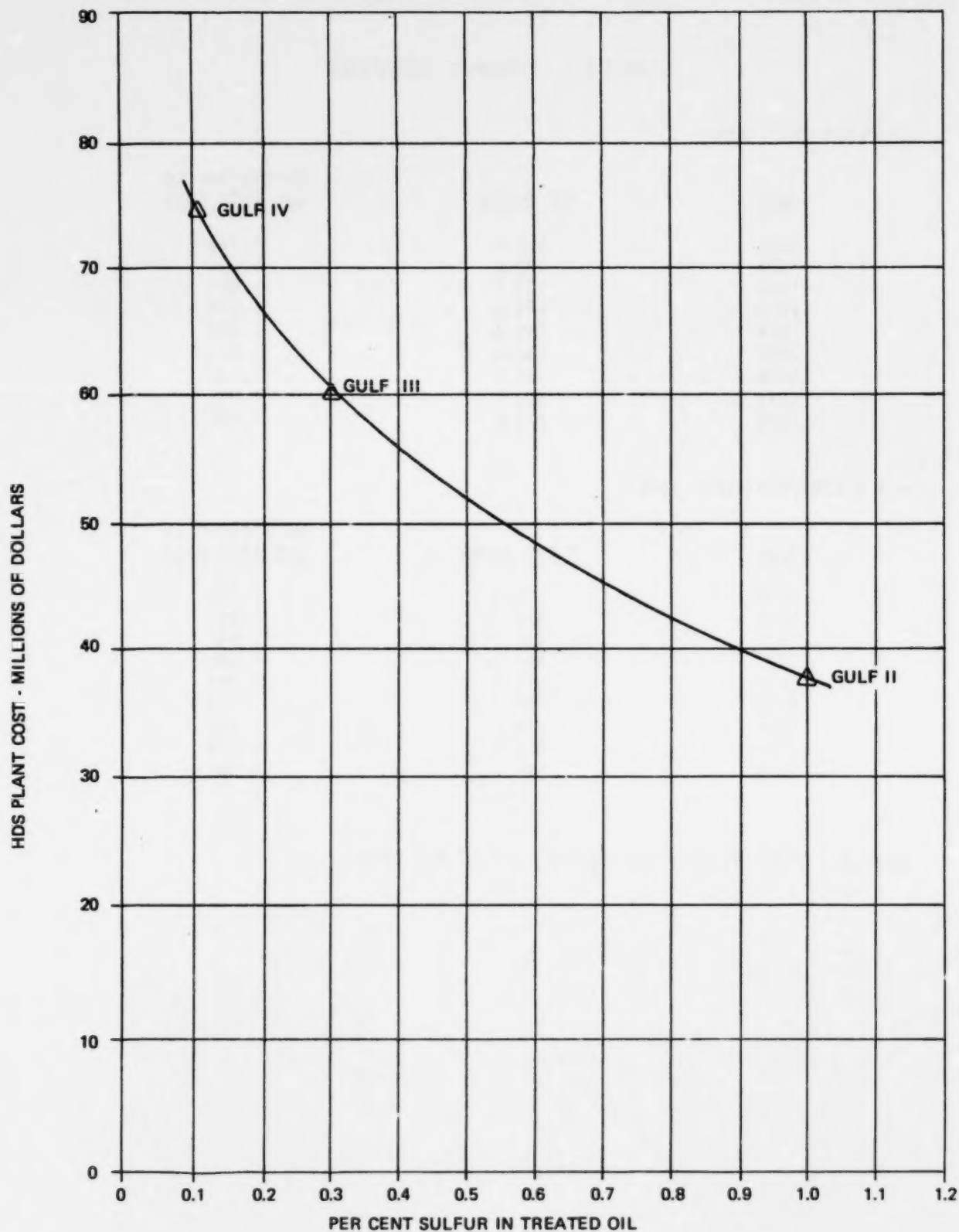
<u>Year</u>	<u>M & S Index</u>	<u>Multiplier to Get 1978 Cost</u>
1970	303.3	1.798
1971	321.3	1.697
1972	332.0	1.642
1973	344.1	1.585
1974	398.4	1.369
1975	444.3	1.228
1976	472.1	1.155
1977	505.4	1.079
1978	545.3	1.000

Source: Chemical Engineering, 86 p. 7, 7 May 1979

Figure 4-7

HDS PLANT COST AS FUNCTION OF SULFUR REMOVAL

Based on Hydrodesulfurization of
50,000 B/D of Kuwait Residual
Fuel Oil Containing 3.8% Sulfur



one-, two-, and three-stage HDS units, as represented by the Gulf II, Gulf III, and Gulf IV processes, respectively.

The selection of these data represents the most widely-reported process in the literature surveyed. The selection of these data is not intended to infer a recommendation or approval of the specific process, and it should be assumed that all similar HDS processes will perform in an equivalent manner.

HDS Unit (Distillate)

Table 4-8 shows similar HDS plant details for the desulfurization of distillate fuel oil.⁽⁵⁾ The Gulf process has again been selected for illustration because of the completeness of the data provided. The investment cost shown has been updated to the June 1978 base.

Hydrogen Plant

Investment costs for the production of hydrogen by the steam reforming of natural gas have been taken from Catalytic's estimating files and are presented in Figure 4-8. These costs have been updated to a June 1978 base and can be expressed as a power relationship by the equation:

where $C = a X^b$

C = installed cost of plant in millions of dollars

X = production capacity of plant in millions of cubic feet
of hydrogen per day

a & b = constants equal to 39.147 and 0.735, respectively

hence $\text{Cost (H}_2\text{ plant)} = 39.147 (\text{capacity})^{0.735}$
in 10^6 dollars in 10^6 SCF/D

Sulfur Plant

Investment cost of Claus-type sulfur recovery plants is given in Figure 4-9 and is taken from the paper "Capital and Operating Costs for 54 Chemical Processes" by K. M. Guthrie of Fluor Corporation as published in the June 15, 1970, issue of Chemical Engineering magazine.⁽⁶⁾ These data have been updated to

TABLE 4-8. DISTILLATE DESULFURIZATION DETAILS

Process	Hydrogen		Catalyst		Utilities		Investment		Feed Sulfur %	Product Sulfur %	Sulfur Removed	
	Usage Scf/BBL	Cost ¢/BBL	Usage lb/BBL	Cost ¢/BBL	Cost ¢/BBL	Capacity B/D	MM \$	0.3% L Ton/Day			0.1% L Ton/Day	
Gulfining	350	56.0	0.01	1.0	10.3	35,000	18.9		2.2	0.2	93.3	103.1

Basis for Calculation of Sulfur Removed:

35,000 B/D distillate fuel oil of 26°API gravity = 0.898 SPGR

Pounds per day of distillate oil = $0.898 \times 8.33 \times 42 \times 35,000$

$$= 11 \times 10^6 \text{ LBS/DAY}$$

$$\text{Tons per day of sulfur removed} = 11 \times 10^6 \left(\frac{\%S_{in} - \%S_{out}}{100} \right) \left(\frac{1}{2240} \right)$$

$$= 49.09 \left(\frac{\%S_{in} - \%S_{out}}{100} \right)$$

Figure 4-8
HYDROGEN PLANT COST
 (Updated to June 1978)

Cost = Capacity 0.735

Where

Cost = Millions of Dollars

Capacity = Millions Cubic Ft. Per Day

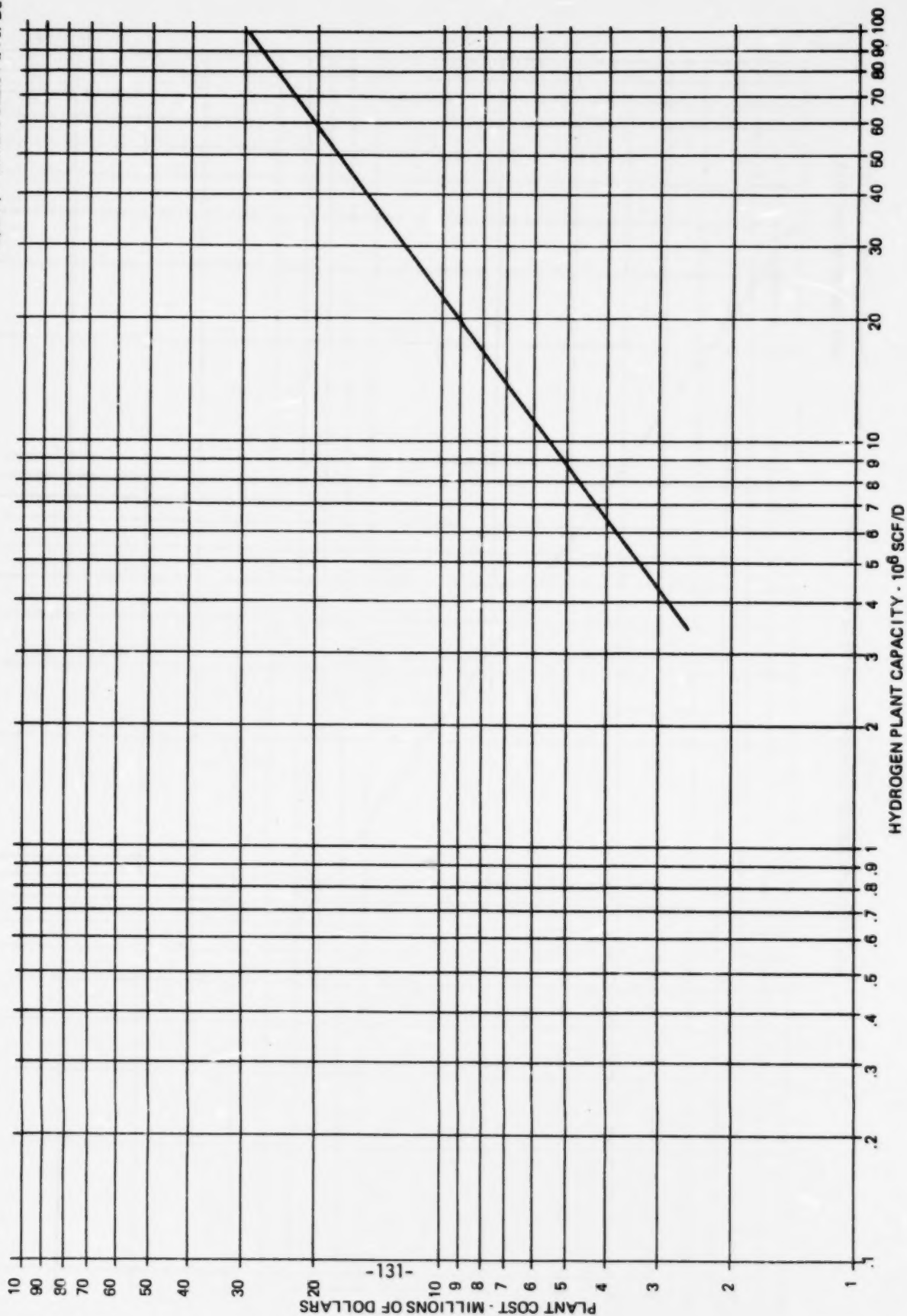
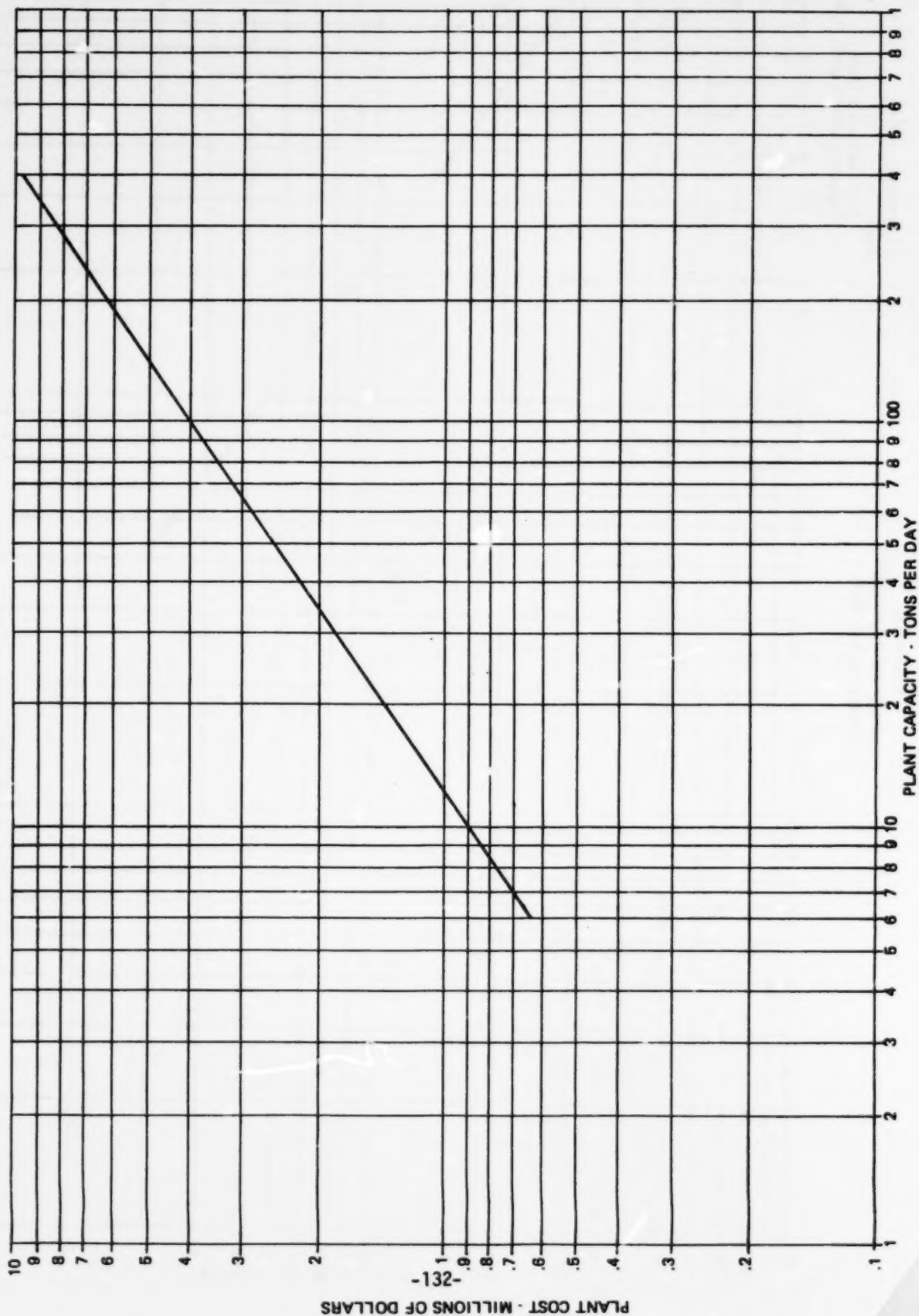


Fig. 4-9

INVESTMENT COST OF CLAUS SULFUR RECOVERY PLANTS

Source - Chem. Engr. P151, June 1970
Costs Updated to June 1978



the June 1978 base and can also be represented by a power relationship of the form:

$$\text{Cost} = a (\text{Capacity})^b$$

where

$$\text{Cost (10}^6 \text{ dollars)} = 0.1877 \times 10^6 (\text{Capacity T/D})^{0.656}$$

This plant cost correlation differs substantially from the cost data given for sulfur recovery plants in the EPA report on proposed performance standards for refinery sulfur recovery plants.⁽⁷⁾ Data from that report give a value of 0.455 for the exponent "b" for the capacity range from 10 to 100 tons per day. The cost relationship developed here is more in agreement with the experience of the senior author, who for years used a power relationship for sulfur plant costs where a value of 0.65 was used for the exponent. The proposed cost correlation is further substantiated by data from Nelson⁽⁸⁾ which give a value of 0.544 for the exponent for capacities ranging from 10 to 100 tons per day and a value of 0.7 for capacities of 100 to 1000 tons per day.

Tail-Gas Treatment Plant

Investment cost of a SCOT tail-gas treatment plant will normally range from 70% to 100% of the cost of the Claus sulfur plant depending upon whether it is integrated and constructed with the Claus plant or is added on at some later date.⁽⁹⁾ For purposes of this study, we have assumed the Claus unit and tail-gas unit would be integral parts of the complete HDS installation and have used a factor of 70% of the sulfur plant cost for the investment cost of the tail-gas unit.

Table 4-9 gives a summary of complete HDS investment costs broken down to show the costs of the HDS unit, hydrogen unit, sulfur unit, and tail-gas treating unit. Costs are summarized for the five types of residual oil and four levels of sulfur control. The tabulated costs are order-of-magnitude costs and have an accuracy of $\pm 25\%$.

TABLE 4-9. HDS PLANT INVESTMENT

<u>Residual Oil</u>	<u>Percent Sulfur in Treated Oil</u>			
	<u>1.6</u>	<u>0.8</u>	<u>0.3</u>	<u>0.1</u>
Ceuta				
HDS Unit	15.0	34.0	54.0	68.0
Hydrogen Unit	3.9	9.4	12.8	14.1
Sulfur Unit	2.1	3.8	4.6	5.0
SCOT Unit	<u>1.4</u>	<u>2.6</u>	<u>3.2</u>	<u>3.5</u>
Total Investment	22.4	49.8	74.6	90.6
East Venezuelan				
HDS Unit	24.0	40.0	58.0	72.0
Hydrogen Unit	5.1	9.9	13.0	14.3
Sulfur Unit	2.7	4.2	5.1	5.4
SCOT Unit	<u>1.9</u>	<u>2.9</u>	<u>3.6</u>	<u>3.8</u>
Total Investment	33.7	57.0	79.7	95.5
Kuwait				
HDS Unit	28.5	42.5	60.0	74.5
Hydrogen Unit	8.4	11.5	13.2	14.0
Sulfur Unit	5.3	6.4	7.1	7.4
SCOT Unit	<u>3.7</u>	<u>4.5</u>	<u>5.0</u>	<u>5.2</u>
Total Investment	45.9	64.9	85.3	101.1
Khafji				
HDS Unit	40.0	48.0	62.0	77.0
Hydrogen Unit	9.3	11.8	13.3	14.1
Sulfur Unit	6.1	7.2	7.8	8.1
SCOT Unit	<u>4.3</u>	<u>5.0</u>	<u>5.5</u>	<u>5.7</u>
Total Investment	59.7	72.0	88.6	104.9
Cold Lake				
HDS Unit	48.5	57.5	70.5	81.0
Hydrogen Unit	9.6	12.2	13.7	14.4
Sulfur Unit	6.4	7.4	8.1	8.3
SCOT Unit	<u>4.5</u>	<u>5.2</u>	<u>5.7</u>	<u>5.8</u>
Total Investment	69.0	82.3	98.0	109.5

NOTE: Plant investments in millions of dollars

Investment Charges

The capital investments presented in Table 4-9 are translated into annual capital charges following the method outlined in Section 5 of the PEDCo report.⁽¹⁰⁾ Based on a useful life of 15 years (which is typical for chemical process units) for the HDS, hydrogen, sulfur, and tail-gas units and an annual interest rate of 10% over the life of the facilities gives a capital recovery factor of approximately 13%. If we add to this a total of 4% of depreciable investment to cover general and administrative costs, taxes, and insurance, we arrive at an annual capital charge of 17% of depreciable investment. This value has been used as the investment charge in this report.

Maintenance Charges

Maintenance charges associated with the upkeep of the physical plant facilities are translated into annual charges by using a factor of 5% of the capital investment costs given in Table 4-9. This factor was also taken from the PEDCo report and covers both maintenance, labor, and materials.

Utility, Labor, and Supervisory Costs

Table 4-10 lists recommended annual unit costs for operating labor and supervision, and various utilities such as cooling water, electricity, fuel, etc. This table has also been taken from the PEDCo report. The PEDCo cost data have been used to provide some degree of consistency so that the cost results obtained in this study can be compared with similar results given in the PEDCo report for other technologies.

Labor

Table 4-11 gives the manning requirements and costs for operating labor and supervision for all the process units.

Hydrogen

Hydrogen consumption for desulfurization of residual fuel oil is calculated from published data⁽¹¹⁾ and is shown in Figure 4-10 as a function of percent

TABLE 4-10. ANNUAL UNIT COSTS FOR OPERATION AND MAINTENANCE
(June 1978 Dollars)

<u>Cost Factors</u>	<u>Recommended Value</u>
Direct labor, \$/man-hour	12.02 ^a
Supervision, \$/man-hour	15.63 ^b
Maintenance, labor, \$/man-hour	14.63 ^a
Electricity, mills/kWh	25.8 ^c
Untreated water, \$/10 ³ gal	0.12 ^d
Process water, \$/10 ³ gal	0.15 ^d
Cooling water, \$/10 ³ gal	0.18 ^e
Boiler feed water, \$/10 ³ gal	1.00 ^f
No. 2 fuel oil, \$/10 ⁶ Btu	3.00 ^g
No. 6 fuel oil, \$/10 ⁶ Btu	2.21 ^g
Natural gas, \$/10 ⁶ Btu	1.95 ^h

^a Engineering News-Record, June 29, 1978, pp. 52-52. Average for Chicago, Cincinnati, Cleveland, Detroit, and St. Louis.

^b Estimated at 30 percent over direct labor rate.

^c EEI members publication for June 1978. Average for Boston, Chicago, Indianapolis, Houston, San Francisco, and Los Angeles.

^d Peters, M. S., and K. D. Timmerhaus, Plant Design and Economics for Chemical Engineers, 2nd Edition, McGraw-Hill Book Co., New York, 1968, p. 772. Adjusted to 1978 prices using Nelson Refinery Operating Cost Indexes for Chemicals, July 1978.

^e Perry, J. H., et al., Chemical Engineer's Handbook, McGraw-Hill Book Co., New York, 1963, pp. 26-29.

^f Nelson, W. L., Guide to Refinery Operating Costs, The Petroleum Publishing Company, 1966, p. 27.

^g Electrical Week, May issues, 1978. Spot market prices.

^h Gas Facts, 1977, American Gas Association. Average U. S. price.

Figure 4-10

CHEMICAL HYDROGEN CONSUMPTION
IN DESULFURIZATION OF 16° API RESIDUAL

Source - Oil & Gas Journal P126 Feb. 28, 1977

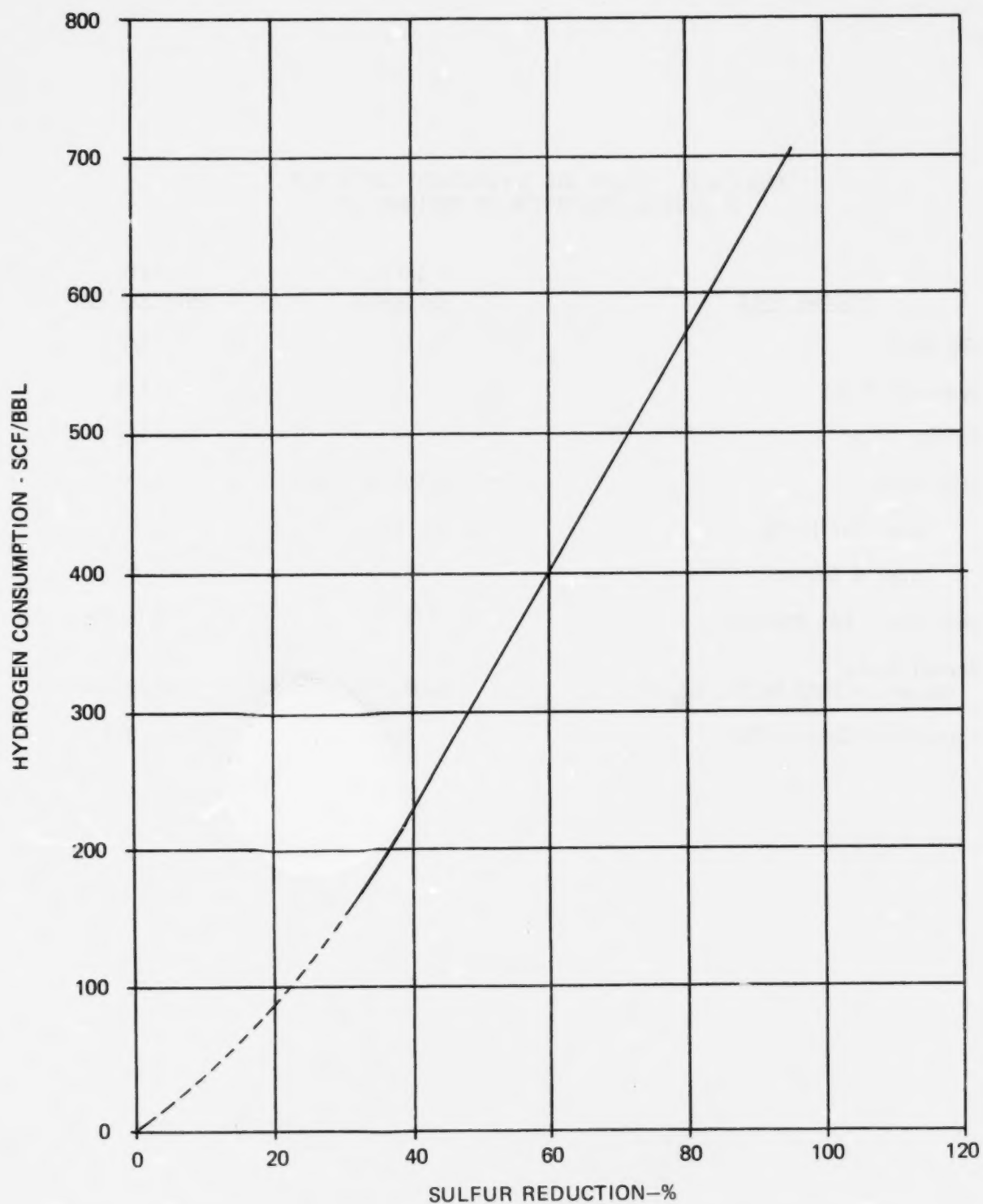


TABLE 4-11. LABOR AND SUPERVISORY COSTS FOR
HYDRODESULFURIZATION OF RESIDUAL OIL

<u>Process Unit</u>	<u>Shift Operators</u>	<u>Shift Supervision</u>
HDS Unit	4	1/2
Hydrogen Plant	1	1/4
Sulfur Plant	1	1/4
SCOT Unit	Incl. w/Sulfur Plant	--
Total Per Shift	6	1
Total 4 Shifts	24	4
Unit Costs Per Manhour	\$12.02	\$15.63
Annual Costs (Based on 2080 MH/Yr Per Man)	\$600,038	\$130,042
Annualized Costs ¢/BBL	3.6	0.8

sulfur reduction. Because of its pronounced effect on the overall cost of hydrodesulfurization, the cost of hydrogen has not been included in the cost of raw materials or utilities, but has been computed as a separate operating cost. Table 4-12 gives the raw material and utility requirements for producing hydrogen and derives a value to be used to determine the cost of hydrogen. The unit costs used in Table 4-12 are taken from Table 4-10. The effect of hydrogen cost on overall hydrodesulfurization costs is discussed in further detail under the sections on cost and sensitivity analysis.

Catalyst

Catalyst consumption for desulfurization of residual fuel oil is calculated from published data.⁽¹²⁾ The cost of catalyst consumed also has a major impact on the overall cost of hydrodesulfurization and is also computed as a separate operating cost. The effect of catalyst cost on overall hydrodesulfurization costs is discussed in further detail in later sections of this report. It should be pointed out that catalyst cost as used herein refers only to the consumption or usage of catalyst and is thereby considered as an operating cost. The cost of the initial charge of catalyst is considered a capital cost and has been included in the HDS unit investment cost.

Waste Treatment

Waste treatment facilities are assumed to represent about 5% of the HDS unit cost.⁽¹³⁾ This is limited to water treatment and does not include provision for catalyst disposal. It is estimated that a similar relationship would exist for the other process units and has so been used in this study.

Catalyst Disposal

For purposes of this study, it has been assumed that spent catalyst will be disposed to landfill with no provision for recovery of any metal values. Because of the toxic nature of the metals absorbed on the catalyst, it is assumed that the catalyst would be sent to a hazardous waste landfill. Quotations received from one company engaged in such hazardous waste disposal gave

TABLE 4-12. HYDROGEN PRODUCTION COSTS

<u>Item</u>	<u>Reqmt's. Per</u> <u>10³ SCF H₂</u>	<u>Unit Cost</u>	<u>Cost Per</u> <u>10³ SCF H₂</u>
Process Feed (Natural Gas)	260 SCF	\$1.95/10 ³ SCF	\$0.51
Fuel (Natural Gas)	415 x 10 ³ BTU	\$1.95/10 ⁶ BTU	0.78
Cooling Water	1450 Gal.	\$0.18/10 ³ Gal.	0.26
Power	1.5 KWH	25.8 Mills/KWH	0.04
Boiler Feedwater	5 Gal.	\$1.00/10 ³ Gal.	<u>0.01</u>
TOTAL			\$1.60

NOTE: Based on steam reforming of natural gas with one stage of CO conversion to produce 95-98% H₂. CO₂ removed by amine scrubbing.

a cost range of \$30 to \$50 per ton of catalyst disposed. This cost includes the cost of transportation of the catalyst to the landfill and the cost of the landfill facility. For purposes of this study, a median cost of \$40 per ton was used. It should be pointed out that recent increases in the cost of metals used in desulfurization have made the recovery of these metals attractive in some cases, and several companies are now engaged in this new business. If this trend continues, it is possible that catalyst disposal may change from an item of cost to an item of return.

Sulfur Recovery

It is assumed that a steady market exists for all sulfur produced and that the sulfur can be sold for a net price of \$25 per long ton.

4.4 SENSITIVITY ANALYSIS

Tables 4-13 through 4-17 give detailed cost breakdowns for the hydrodesulfurization of five residual fuel oils for four levels of sulfur in the desulfurized oils. Table 4-18 gives a similar breakdown for the desulfurization of distillate fuel oil to two levels of sulfur in the treated oil.

A most striking statistic to be gathered from these tables is that of the ten cost elements listed; five of these have a very minor effect on the overall cost of desulfurization. These five items - waste treatment, catalyst disposal, labor, supervision, and overhead - exert a cumulative effect of less than ten percent (10%) on the overall cost and, in fact, ranges to as low as three percent (3%) in some cases. For this reason, we will concentrate our analysis and discussion on the other five cost elements; namely, investment charges, maintenance charges, utilities costs, hydrogen cost, and catalyst costs.

Investment Charges

As might be expected, investment charges have a major impact on the overall cost of desulfurization ranging from 17% to nearly 29% of the overall costs. This is easily understood when one realizes that a complete 50,000 B/D hydrodesulfurization unit consists not only of the HDS unit but also of a hydrogen

TABLE 4-13. TOTAL COST OF HYDRODESULFURIZATION OF RESIDUAL FUEL OIL

Based on 50,000 B/SD Residual Oil Feed
 Residual Type: Ceuta
 Containing 2.12% S and 292 ppm (Ni + V)

<u>Cost Item</u>	<u>Cost Per Barrel of Treated Oil for Following % S in Treated Oil</u>			
	<u>1.6%</u>	<u>0.8%</u>	<u>0.3%</u>	<u>0.1%</u>
Investment Charge	23.1¢/BBL	51.3¢/BBL	76.9 ¢/BBL	93.3 ¢/BBL
Maintenance Charge	6.8	15.1	22.6	27.5
Utilities Cost	24.9	49.7	62.0	65.7
Hydrogen Cost	21.0	67.0	102.0	117.0
Catalyst Cost	9.0	38.0	121.0	216.0
Waste Treatment	1.5	3.3	5.0	6.0
Catalyst Disposal	0.1	0.4	1.3	2.8
Labor	3.6	3.6	3.6	3.6
Supervision	0.8	0.8	0.8	0.8
Overhead	<u>2.5</u>	<u>2.5</u>	<u>2.5</u>	<u>2.5</u>
TOTAL	93.3	231.7	397.7	535.2
Sulfur Credit	2.0	5.0	6.9	7.6
NET COST	91.3 (\$0.91)	226.7 (\$2.28)	390.8 (\$3.91)	527.6 (\$5.28)

NOTES: Investment charge at 17% of total plant investment.
 Maintenance charge at 5% of total plant investment.
 Waste treatment at 1.1% of total plant investment.
 Overhead at 56% of labor plus supervision cost.
 Sulfur credit at \$25 per ton of sulfur recovered.

TABLE 4-14. TOTAL COST OF HYDRODESULFURIZATION OF RESIDUAL FUEL OIL

Based on 50,000 B/SD Residual Oil Feed
 Residual Type: East Venezuelan
 Containing 2.38% S and 274 ppm (Ni + V)

<u>Cost Item</u>	<u>Cost Per Barrel of Treated Oil for Following % S in Treated Oil</u>			
	<u>1.6%</u>	<u>0.8%</u>	<u>0.3%</u>	<u>0.1%</u>
Investment Charge	34.7¢/BBL	58.7¢/BBL	82.1 ¢/BBL	98.4 ¢/BBL
Maintenance Charge	10.2	17.3	24.2	28.9
Utilities Cost	24.9	49.7	62.0	65.7
Hydrogen Cost	29.0	73.0	104.0	118.0
Catalyst Cost	12.0	41.0	115.0	252.0
Waste Treatment	2.2	3.8	5.3	6.4
Catalyst Disposal	0.1	0.4	1.3	2.8
Labor	3.6	3.6	3.6	3.6
Supervision	0.8	0.8	0.8	0.8
Overhead	<u>2.5</u>	<u>2.5</u>	<u>2.5</u>	<u>2.5</u>
TOTAL	120.0	250.8	400.8	579.1
Sulfur Credit	3.0	6.0	7.8	8.6
NET COST	117.0 (\$1.17)	244.8 (\$2.45)	393.0 (\$3.93)	570.5 (\$5.71)

NOTES: Investment charge at 17% of total plant investment.
 Maintenance charge at 5% of total plant investment.
 Waste treatment at 1.1% of total plant investment.
 Overhead at 56% of labor plus supervision cost.
 Sulfur credit at \$25 per ton of sulfur recovered.

TABLE 4-15. TOTAL COST OF HYDRODESULFURIZATION OF RESIDUAL FUEL OIL

Based on 50,000 B/SD Residual Oil Feed
Residual Type: Kuwait
Containing 3.8% S and 60 ppm (Ni + V)

<u>Cost Item</u>	<u>Cost Per Barrel of Treated Oil for Following % S in Treated Oil</u>			
	<u>1.6%</u>	<u>0.8%</u>	<u>0.3%</u>	<u>0.1%</u>
Investment Charge	47.3 ¢/BBL	66.9 ¢/BBL	87.9 ¢/BBL	104.2 ¢/BBL
Maintenance Charge	13.9	19.7	25.8	30.6
Utilities Cost	47.8	59.4	73.4	76.9
Hydrogen Cost	58.0	88.0	107.0	115.0
Catalyst Cost	11.0	15.0	20.0	24.0
Waste Treatment	3.1	4.3	5.7	6.7
Catalyst Disposal	0.1	0.2	0.2	0.3
Labor	3.6	3.6	3.6	3.6
Supervision	0.3	0.8	0.8	0.8
Overhead	<u>2.5</u>	<u>2.5</u>	<u>2.5</u>	<u>2.5</u>
TOTAL	188.1	260.4	326.9	364.6
Sulfur Credit	8.3	11.3	13.2	13.9
NET COST	179.8 (\$1.80)	249.1 (\$2.49)	313.7 (\$3.14)	350.7 (\$3.51)

NOTES: Investment charge at 17% of total plant investment.
Maintenance charge at 5% of total plant investment.
Waste treatment at 1.1% of total plant investment.
Overhead at 56% of labor plus supervision cost.
Sulfur credit at \$25 per ton of sulfur recovered.

TABLE 4-16. TOTAL COST OF HYDRODESULFURIZATION OF RESIDUAL FUEL OIL

Based on 50,000 B/SD Residual Oil Feed
 Residual Type: Khafji
 Containing 4.36% S and 118 ppm (Ni + V)

<u>Cost Item</u>	<u>Cost Per Barrel of Treated Oil for Following % S in Treated Oil</u>			
	<u>1.6%</u>	<u>0.8%</u>	<u>0.3%</u>	<u>0.1%</u>
Investment Charge	61.5¢/BBL	74.2 ¢/BBL	91.3 ¢/BBL	108.1 ¢/BBL
Maintenance Charge	18.1	21.8	26.8	31.8
Utilities Cost	54.2	64.8	80.4	82.9
Hydrogen Cost	66.0	92.0	109.0	117.0
Catalyst Cost	19.0	33.0	54.0	72.0
Waste Treatment	4.0	4.8	5.9	7.0
Catalyst Disposal	0.2	0.4	0.6	0.8
Labor	3.6	3.6	3.6	3.6
Supervision	0.8	0.8	0.8	0.8
Overhead	<u>2.5</u>	<u>2.5</u>	<u>2.5</u>	<u>2.5</u>
TOTAL	229.9	297.9	374.9	426.5
Sulfur Credit	10.4	13.4	15.3	16.0
NET COST	219.5 (\$2.20)	284.5 (\$2.85)	359.6 (\$3.60)	410.5 (\$4.11)

NOTES: Investment charge at 17% of total plant investment.
 Maintenance charge at 5% of total plant investment.
 Waste treatment at 1.1% of total plant investment.
 Overhead at 56% of labor plus supervision cost.
 Sulfur credit at \$25 per ton of sulfur recovered.

TABLE 4-17. TOTAL COST OF HYDRODESULFURIZATION OF RESIDUAL FUEL OIL

Based on 50,000 B/SD Residual Oil Feed
Residual Type: Cold Lake
Containing 4.55% S and 236 ppm (Ni + V)

<u>Cost Item</u>	<u>Cost Per Barrel of Treated Oil for Following % S in Treated Oil</u>			
	<u>1.6%</u>	<u>0.8%</u>	<u>0.3%</u>	<u>0.1%</u>
Investment Charge	71.1 ¢/BBL	84.8 ¢/BBL	101.1 ¢/BBL	112.8 ¢/BBL
Maintenance Charge	21.0	24.9	30.6	34.2
Utilities Cost	54.2	64.8	80.4	82.9
Hydrogen Cost	70.0	96.0	113.0	120.0
Catalyst Cost	35.0	72.0	129.0	234.0
Waste Treatment	4.6	5.5	6.5	7.3
Catalyst Disposal	0.4	0.8	1.4	2.6
Labor	3.6	3.6	3.6	3.6
Supervision	0.8	0.8	0.8	0.8
Overhead	<u>2.5</u>	<u>2.5</u>	<u>2.5</u>	<u>2.5</u>
TOTAL	263.2	355.7	468.8	600.7
Sulfur Credit	11.1	14.1	16.0	16.7
NET COST	252.1 (\$2.52)	341.6 (\$3.42)	452.8 (\$4.53)	584.0 (\$5.84)

NOTES: Investment charge at 17% of total plant investment.
Maintenance charge at 5% of total plant investment.
Waste treatment at 1.1% of total plant investment.
Overhead at 56% of labor plus supervision cost.
Sulfur credit at \$25 per ton of sulfur recovered.

TABLE 4-18. COST OF HYDRODESULFURIZATION OF DISTILLATE FUEL OIL
(Basis: 35,000 B/D)

<u>Item</u>	<u>Fuel Oil Sulfur</u>	
	<u>0.3%</u>	<u>0.1%</u>
	<u>¢/BBL</u>	<u>¢/BBL</u>
Hydrogen	47.7	58.8
Catalyst	1.0	1.0
Utilities	9.8	10.8
Investment Charge	44.5	48.7
Maintenance Charge	13.1	14.3
Catalyst Disposal	0.1	0.1
W. Water Treatment	2.9	3.1
Labor	5.1	5.1
Supervision	1.2	1.2
Overhead (56%)	<u>3.5</u>	<u>3.5</u>
Total	128.9	146.6
Less Sulfur Credit	<u>6.7</u>	<u>7.4</u>
Net Cost	122.2 (\$1.22)	139.2 (\$1.39)
Total Plant Investment		
HDS Unit	\$ 18 x 10 ⁶	\$19.8 x 10 ⁶
Hydrogen Plant	6 x 10 ⁶	6.5 x 10 ⁶
Sulfur Plant	3.7 x 10 ⁶	4.0 x 10 ⁶
SCOT Unit	<u>2.6 x 10⁶</u>	<u>2.8 x 10⁶</u>
TOTAL	\$30.3 x 10 ⁶	\$33.1 x 10 ⁶

plant with capacities ranging from six million cubic feet per day (6×10^6 SCFD) to nearly thirty-eight million cubic feet per day (38×10^6 SCFD) and a sulfur plant and tail gas unit with capacities ranging from nearly forty tons per day (40 T/D) to more than three hundred thirty tons per day (330 T/D). These are large and expensive plants.

Another interesting fact to be noted from these tables is that the investment charges increase quite rapidly with the degree of desulfurization. This is brought about by the fact that going to higher degrees of desulfurization, or lower levels of sulfur in the treated oil, requires more and more stages of desulfurization. For example, one stage of desulfurization is usually sufficient to obtain an oil of 0.8% sulfur, whereas two stages are required to get 0.3% sulfur and three stages are required for 0.1% sulfur. This effect of staging on cost is perhaps better shown in Table 4-6, which gives the capital investment of the HDS units in dollars rather than annualized costs per barrel. This table clearly shows the jumps in investment in going from one to two to three stages of desulfurization.

Maintenance Charges

Maintenance charges also play a major role in the overall cost of desulfurization ranging from 5 to 8.5% of the overall cost. As might be expected, the maintenance charges parallel the investment charges, since they are simply a fixed percentage of investment.

Utilities Cost

Utility consumption and costs are presented in Table 4-19. As presented here, utility costs are relatively independent of feed sulfur level but are directly sensitive to the degree of sulfur removal. For this reason, the data is presented on the basis of low, medium, and high sulfur levels corresponding to less than 3% S, 3-4% S, and more than 4% S. Thus, the Ceuta and E. Venezuelan residuals fall under the low sulfur category, the Kuwait residual under the medium, and the Khafji and Cold Lake residuals are classified as high sulfur

TABLE 4-19. UTILITY CONSUMPTION AND COST

Crude Class	Utility	Unit Costs	Sulfur in Fuel Oil							
			1.6		0.8		0.3		0.1	
			Usage	Cost ¢/BBL	Usage	Cost ¢/BBL	Usage	Cost ¢/BBL	Usage	Cost ¢/BBL
Low Sulfur <3% S	Power	25.8 Mils/KWH	2.7	7.0	5.7	14.7	7.2	18.6	7.6	19.6
	Steam	\$3.15 x 10 ⁻⁶ BTU	12.8	4.0	28.3	8.9	44.4	14.0	48.6	15.3
	Fuel	\$2.91 x 10 ⁻⁶ BTU	43.0	12.5	82.0	23.9	92.3	26.9	96.0	27.9
	Cooling Water	\$0.18/MGal	0.08	1.4	0.12	2.2	0.14	2.5	0.16	2.9
	Total Cost			24.9		49.7		62.0		65.7
Med. Sulfur 3-4% S	Power	25.8 Mils/KWH	5.3	13.7	6.9	17.8	9.0	23.2	9.4	24.3
	Steam	\$3.15 x 10 ⁻⁶ BTU	31.0	9.8	43.8	13.8	63.8	20.1	71.2	22.4
	Fuel	\$2.91 x 10 ⁻⁶ BTU	76.0	22.1	87.0	25.3	94.0	27.4	94.3	27.5
	Cooling Water	\$0.18/MGal	0.12	2.2	0.14	2.5	0.15	2.7	0.15	2.7
	Total Cost			47.8		59.4		73.4		76.9
High Sulfur >4% S	Power	25.8 Mils/KWH	6.4	16.5	8.0	20.6	9.7	25.0	9.9	25.5
	Steam	\$3.15 x 10 ⁻⁶ BTU	37.4	11.8	49.2	15.5	79.6	25.1	84.4	26.6
	Fuel	\$2.91 x 10 ⁻⁶ BTU	81.0	23.6	90.0	26.2	95.0	27.6	96.0	27.9
	Cooling Water	\$0.18/MGal	0.13	2.3	0.14	2.5	0.15	2.7	0.16	2.9
	Total Cost			54.2		64.8		80.4		82.9

NOTE: Utility Units

Power in KWH/Bbl
 Steam in MBTU/Bbl
 Fuel in MBTU/Bbl
 Cooling Water in MGal/Bbl

oils. One important item of Table 4-19 is that it does not include the utilities associated with the production of hydrogen but does include all power, steam, fuel, and cooling water used in the desulfurization unit, and the sulfur recovery and tail-gas units. The consumption and cost of hydrogen has such an appreciable impact on the overall cost of desulfurization that hydrogen cost is treated as a separate cost element in our cost analysis.

Even without the hydrogen utilities, the cost of utilities is a major cost element ranging from about 12% to more than 25% of the overall desulfurization costs.

Hydrogen Cost

Hydrogen usage is primarily a function of the sulfur and asphaltene content of the residuum fed to the HDS unit. As seen in Tables 4-13 through 4-18 at S.I.P. (1.6%) and moderate (0.8%) sulfur levels, hydrogen represents the most important variable cost in the overall cost picture. Table 4-20 gives hydrogen consumption and cost for desulfurization of the five residual fuel oils to the four control levels of sulfur.

As seen in Table 4-20, hydrogen usage varies almost directly with the degree of desulfurization. Hence, although the cost of hydrogen is a major cost element at all levels of desulfurization, the impact on overall cost is somewhat reduced at higher degrees of sulfur removal or lower sulfur levels. For example, the cost of hydrogen to desulfurize a Ceuta residua to the moderate level of control (0.8% S) is \$0.67/bbl or 28.9% of the total cost of desulfurization; whereas, to desulfurize the same residua to the intermediate level of control (0.3% S) and stringent level of control (0.1%) results in hydrogen costs of \$1.02/bbl or 25.6% of the total and \$1.17/bbl or 21.9% of the total, respectively.

Catalyst Cost

Catalyst usage is an exponential function of the degree of sulfur removal and the metal (primarily Ni + V) content of the residuum feed. Table 4-21 gives

TABLE 4-20. HYDROGEN CONSUMPTION AND COST FOR DESULFURIZATION OF RESIDUAL FUEL OIL

Residual Oil		Percent Sulfur in Residual Oil							
Source	% S	1.6		0.8		0.3		0.1	
		% S Removal	H ₂ Use SCF/BBL	% S Removal	H ₂ Use SCF/BBL	% S Removal	H ₂ Use SCF/BBL	% S Removal	H ₂ Use SCF/BBL
Ceuta 292 ppm (V + Ni)	2.12	24.5	128 (\$0.21)	62.3	418 (\$0.67)	85.8	638 (\$1.02)	95.3	728 (\$1.17)
E. Venezuelan 274 ppm (V + Ni)	2.38	32.8	184 (\$0.29)	66.4	454 (\$0.73)	87.4	651 (\$1.04)	95.8	735 (\$1.18)
Kuwait 160 ppm (V + Ni)	3.80	57.9	365 (\$0.58)	78.9	549 (\$0.88)	92.1	666 (\$1.07)	97.4	720 (\$1.15)
Khafji 118 ppm (V + Ni)	4.36	63.3	414 (\$0.66)	81.7	576 (\$0.92)	93.1	680 (\$1.09)	97.7	729 (\$1.17)
Cold Lake 236 ppm (V + Ni)	4.55	64.8	436 (\$0.70)	82.4	599 (\$0.96)	93.4	705 (\$1.13)	97.8	751 (\$1.20)

NOTE: Hydrogen costs are shown in parentheses under hydrogen use and are based on cost of \$1.60 per 103 SCF.

TABLE 4-21. CATALYST CONSUMPTION AND COST FOR DESULFURIZATION OF RESIDUAL FUEL OIL

Residual Oil		Percent Sulfur in Residual Oil							
Source	% S	1.6		0.8		0.3		0.1	
		% S Removal	Catalyst Use LBS/BBL	% S Removal	Catalyst Use LBS/BBL	% S Removal	Catalyst Use LBS/BBL	% S Removal	Catalyst Use LBS/BBL
Ceuta 292 ppm (V + Ni)	2.12	24.5	0.51 (\$0.09)	62.3	0.21 (\$0.38)	85.8	0.67 (\$1.21)	95.3	1.2 (\$2.16)
E. Venezuelan 1,274 ppm (V + Ni)	2.38	32.8	0.069 (\$0.12)	66.4	0.227 (\$0.41)	87.4	0.637 (\$1.15)	95.8	1.4 (\$2.52)
Kuwait 60 ppm (V + Ni)	3.80	57.9	0.06 (\$0.11)	78.9	0.083 (\$0.15)	92.1	0.11 (\$0.20)	97.4	0.135 (\$0.24)
Khafji 118 ppm (V + Ni)	4.36	63.3	0.105 (\$0.19)	81.7	0.182 (\$0.33)	93.1	0.30 (\$0.54)	97.7	0.40 (\$0.72)
Cold Lake 236 ppm (V + Ni)	4.55	64.8	0.192 (\$0.35)	82.4	0.40 (\$0.72)	93.4	0.714 (\$1.29)	97.9	1.3 (\$2.34)

NOTE: Catalyst costs are shown in parentheses under catalyst use and are based on cost of \$1.80 per pound.

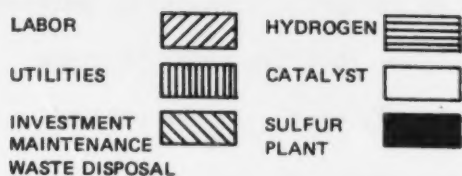
the catalyst consumption and cost for desulfurization of the five selected residual fuel oils and the four control levels of sulfur. It should be pointed out that this table represents a worse case basis in that the catalyst usage was calculated on the basis of no guard reactor being used. In the case of high metal feeds or severe desulfurization to extremely low levels such as 0.1% S, a refinery would probably use a guard reactor for removing metals which would reduce the desulfurization catalyst usage and cost by perhaps 25-30%.

As seen from Tables 4-13 through 4-18, catalyst costs vary more than any other cost element, ranging from a low of \$0.09/bbl or 9.6% of the total cost for desulfurization of a low sulfur Ceuta residua to a high of \$2.52/bbl or 43.5% of the total cost for desulfurization of a high metal (274 ppm Ni + V) E. Venezuelan residual. It is also evident from Tables 4-13 through 4-17 that desulfurization to S.I.P. (1.6% S) or moderate (0.8% S) levels of control result in modest catalyst costs ranging from \$0.11/bbl or 5.8% to \$0.15/bbl or 5.8% for desulfurization of a low metals Kuwait residual to these sulfur levels. These tables dramatically show the effect of metal content as the degree of desulfurization or level of control approaches the intermediate control level of 0.3% S. At this level, catalyst usage begins to dominate the cost profile, except for the low metal feedstocks. At stringent levels of desulfurization (0.1% S), the metal content becomes of prime importance; and, in the case of high metal feedstocks such as the Ceuta and E. Venezuelan feeds, can become the highest single cost element.

Figures 4-11 and 4-12 vividly illustrate the relative importance of the above cost segments. Figure 4-11 gives the cost distribution for the desulfurization of three residua to S.I.P. (1.6%) and moderate (0.8%) sulfur levels, whereas Figure 4-12 presents similar information for desulfurization to intermediate (0.3%) and stringent (0.1%) sulfur levels.

Figure 4-11

COST DISTRIBUTION FOR DESULFURIZATION OF
THREE RESIDUA TO MODERATE SULFUR LEVELS



*Sulfur Plant Operations Result in Net Credit
Note: Figures Show % of Total Cost for Each Element

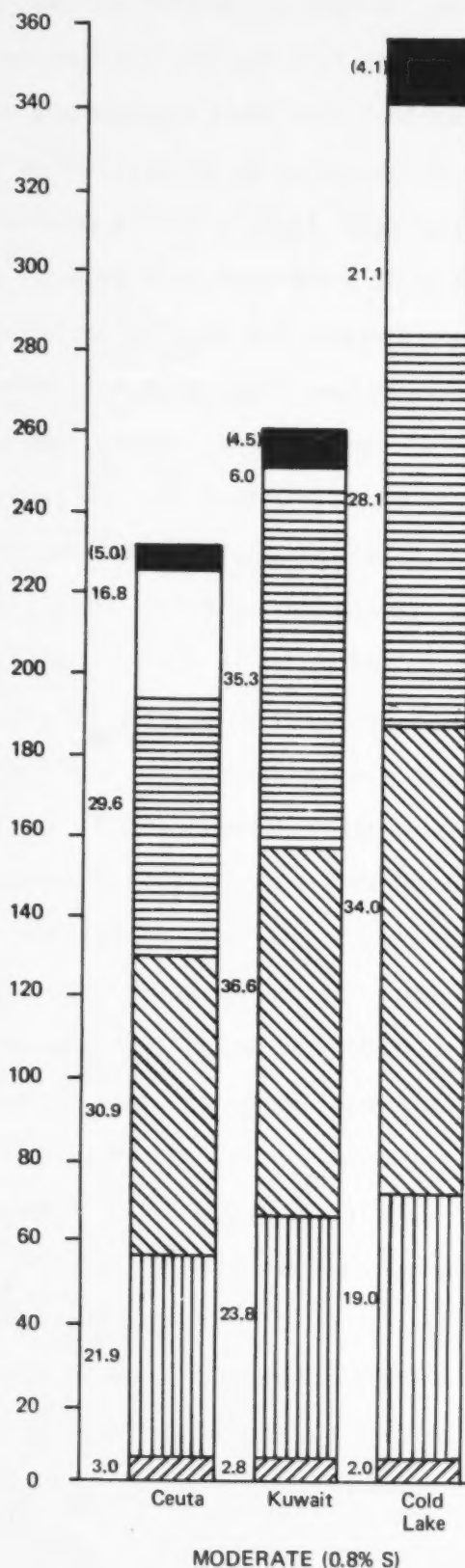
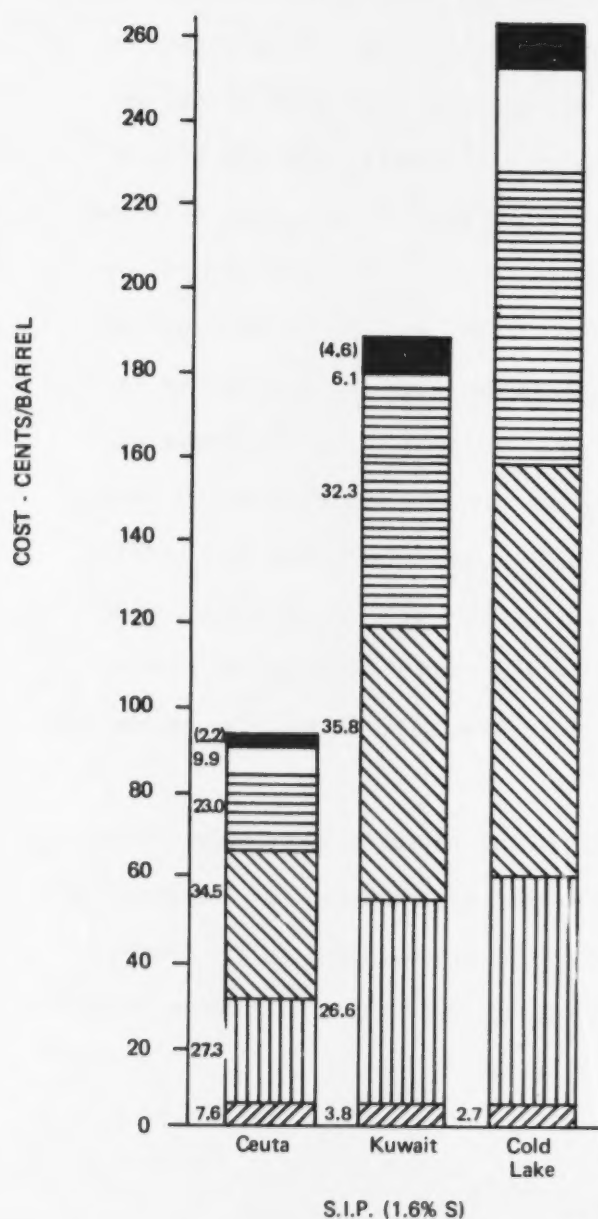
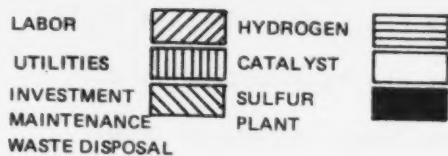
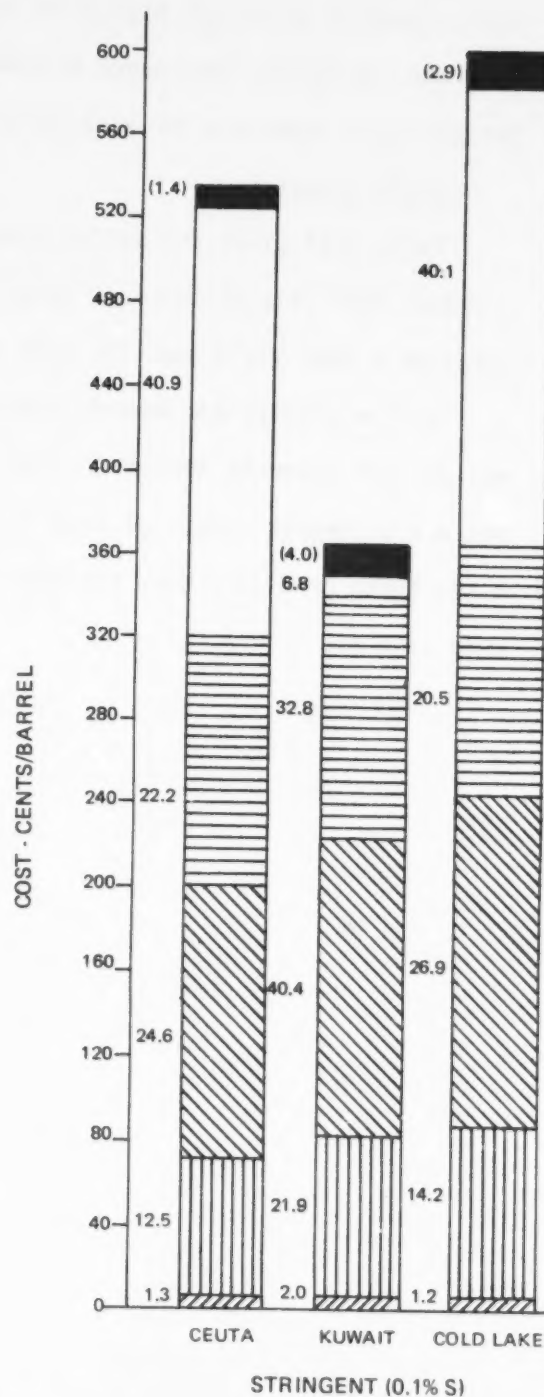
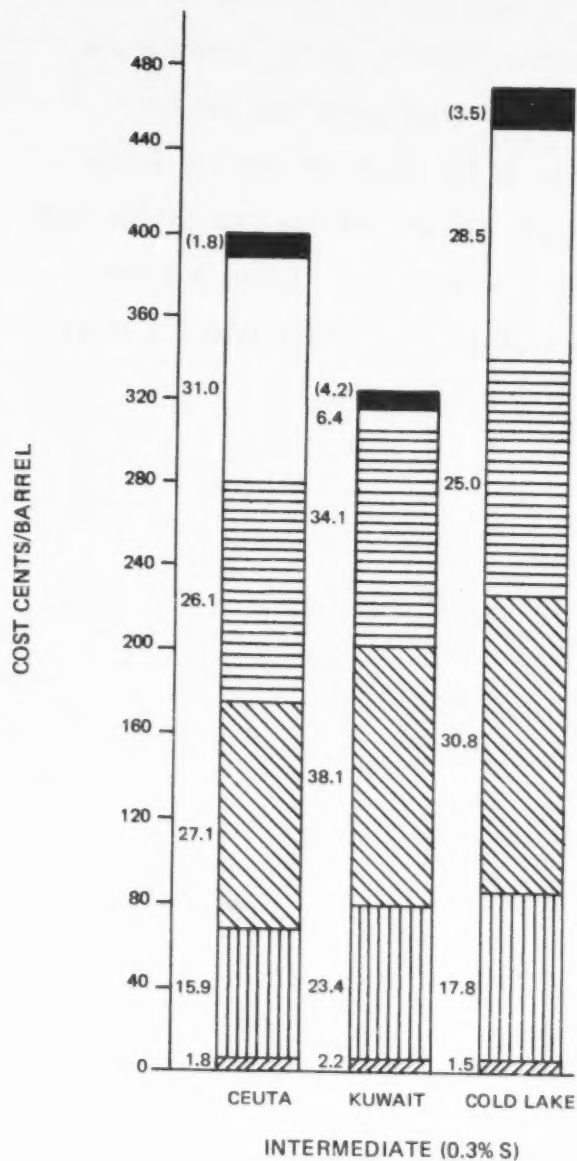


Figure 4-12

COST DISTRIBUTION FOR DESULFURIZATION OF
THREE RESIDUA TO INTERMEDIATE & STRINGENT SULFUR LEVELS



* Sulfur Plant Operations Result in Net Credit
Note: Figures Show % of Total Cost for Each Element



The extreme effect of catalyst consumption is clearly shown in these figures by comparing the low-metals Kuwait figures to the Ceuta and Cold Lake residuals, both of which are high-metal feedstocks. These charts also clearly demonstrate the lesser importance of catalyst cost at the lower degrees of desulfurization or moderate to high levels of control.

Sulfur Credits

Table 4-22 gives the sulfur removal (in long tons per day) for the five residual fuel oils at the four selected control levels. Sulfur removals are based on a 100% yield and, for cost purposes, is credited at \$25 per ton.

Sulfur credits are modest, ranging from as low as 2¢/bbl for low sulfur residua and moderate desulfurization to nearly 17¢/bbl for the high sulfur residua and stringent levels of desulfurization. As seen from Figures 4-11 and 4-12, these credits reduce the overall cost of desulfurization from 2.2 to as much as 4.6%.

TABLE 4-22. SULFUR REMOVAL FOR VARIOUS CONTROL LEVELS
BASED ON 50,000 B/D RESIDUAL FUEL OIL

Residual Oil		Tons/Day Sulfur Removed For Various % S _{Out}							
Source	% S _{In}	1.6		0.8		0.3		0.1	
		ΔS	T/D	ΔS	T/D	ΔS	T/D	ΔS	T/D
Ceuta	2.12	0.52	39.1	1.32	99.2	1.82	136.7	2.02	151.8
E. Venezuela	2.38	0.78	58.6	1.58	118.7	2.08	156.3	2.28	171.3
Kuwait	3.80	2.20	165.3	3.00	225.4	3.50	263.0	3.70	278.0
Khafji	4.36	2.76	207.4	3.56	267.5	4.06	305.0	4.26	320.1
Cold Lake	4.55	2.95	221.6	3.75	281.8	4.25	319.3	4.45	334.3

Basis for calculation 50,000 B/D residual fuel oil of 15.7°API gravity (0.961 SP. Gr.)

$$\begin{aligned}\text{Pounds/day of fuel oil} &= 0.961 \times 8.33 \times 42 \times 50,000 \\ &= 16.81 \times 10^6\end{aligned}$$

$$\begin{aligned}\text{Tons/day of sulfur removed} &= 16.81 \times 10^6 \left(\frac{\% S_{In} - \% S_{Out}}{100} \right) \left(\frac{1}{2240} \right) \\ &= 75.04 (\% S_{In} - \% S_{Out})\end{aligned}$$

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4.5

APPENDIX - SAMPLE CALCULATIONS

The following calculations are based on the desulfurization of Kuwait residuum to a 0.1% product sulfur level and are presented here to illustrate the bases and methods of calculations used in this report.

1. Per Cent Desulfurization

$$\% \text{ Desulfurization} = \frac{\% S_{in} - \% S_{out}}{\% S_{in}} \times 100$$

$$\% \text{ Desulfurization} = \frac{3.8 - 0.1}{3.8} \times 100 = 97.4\%$$

2. Hydrogen Usage and Cost

From Ref 1. API gravity = 15.7°

From Ref. 11, Fig. 1

For API gravity of 15.7° and 97.4% sulfur removal the base hydrogen consumption = 810 SCF/Bbl

Packed bed credit = 9%

Correction for metals content = -2% hence:

$$\begin{aligned} \text{Corrected H}_2 \text{ consumption} &= 810 \times 0.91 \times 0.98 \\ &= 720 \text{ SCF/Bbl} \end{aligned}$$

$$\begin{aligned} \text{Hydrogen cost @ } \$1.60/10^3\text{SCF} &= \frac{\$1.60 \times 720}{10^3} \\ &= \$1.15 \end{aligned}$$

3. Catalyst Usage and Cost

From Ref. 12 Fig. 1

At 97.4% sulfur removal and 60ppm metals in the feed

Barrels feed/# catalyst = 7.4

$$\text{or lbs. catalyst consumed per barrel feed} = \frac{1}{7.4} = 0.135$$

$$\text{Catalyst cost @ } \$1.80/\text{lb.} = \$1.80 \times 0.135 = \$0.24$$

4. Investment Charges

From Table 4-9

Total Investment at 0.1 % S = $\$101.1 \times 10^6$

Investment Charge @ 17%/yr.

$$= \frac{\$101.1 \times 10^6 \times 0.17 \times 100}{50,000 \times 330}$$

$$= \$1.042/\text{Bbl.}$$

5. Maintenance Charges

At 5% of investment

$$\text{Maintenance charge} = \frac{\$101.1 \times 10^6 \times 0.05 \times 100}{50,000 \times 330}$$

$$= \$0.306$$

6. Sulfur Plant Costs

From Ref. 1 API gravity = 15.7⁰

$$\text{Specific gravity} = \frac{141.5}{131.5 + 15.7} = 0.961$$

$$\% \text{ sulfur in} = 3.8\%$$

$$\% \text{ sulfur out} = 0.1\%$$

$$\text{Sulfur removal} = \frac{3.8 - 0.1}{100} \times \frac{(0.961)(8.33)(42)(50000)}{2240}$$

$$= 277.7 \text{ tons/day}$$

From Fig. 4-9

$$\text{Sulfur plant cost} = \$7.5 \times 10^6$$

Check cost by use of equation

$$C = 0.1877 \times (\text{capacity})^{0.656}$$

$$C = 0.1877 \times (277.7)^{0.656}$$

$$C = \$7.56 \times 10^6$$

7. Sulfur Credit

at \$25/ton

$$\text{Sulfur credit} = \frac{277.7 \times 25}{50000} = \$0.139/\text{Bbl.}$$

8. Waste Disposal Charges

Basis 1.1% of Total Plant Investment

$$\text{Cost} = \frac{0.011 \times \$101.1 \times 10^6}{50000 \times 330}$$

$$= \$ 0.067/\text{Bbl.}$$

9. Labor, Supervision and Overhead

a) Labor

$$\text{Men/shift} = 6$$

$$\text{No. shifts} = 4$$

$$\text{Unit cost per manhour} = \$12.02$$

$$\text{Annual Cost} = \frac{4 \times 6 \times 40 \times 52 \times \$12.02}{50000 \times 330}$$

$$= \$ 0.036/\text{Bbl.}$$

b) Supervision

Basis 1 man/shift, 4 shifts and \$15.63 per manhour.

$$\text{Cost} = \frac{1 \times 4 \times 40 \times 52 \times 15.63}{50000 \times 330}$$

$$= \$ 0.008/\text{Bbl.}$$

c) Overhead

Basis - Payroll overhead 30% of (a + b)

Plant overhead 26% of (a + b)

or total of 56% of (a + b)

$$\text{Cost} = 0.56 \times (\$0.036 + \$0.008)$$

$$= 0.56 \times \$0.044$$

$$= \$0.025$$

10. Fuel Oil Costs

Basis: Residual Fuel Oil Gravity 22.00API

Gross Heat of Combustion 19,000 BTU/lb.

Cost = \$2.21/10⁶ BTU (PEDCo)

Distillate Fuel Oil Gravity 26.00API

Gross Heat of Combustion 19,200 BTU/lb.

Cost = 3.00/10⁶ BTU (PEDCo)

NOTE: Gravities are typical of source data

Gross heats from API data

a) Residual Fuel Oil Specific Gravity

$$\begin{aligned} \text{S.G.} &= \frac{141.5}{131.5 + 22.0} \\ &= 0.922 \end{aligned}$$

b) Residual Fuel Oil Heat Content

$$\begin{aligned} \text{Heat Content} &= 0.922 (8.33) (42) (19,000) \\ &= 6,135,000 \text{ BTU/BB1} \end{aligned}$$

c) Residual Fuel Oil Cost

$$\begin{aligned} \text{Cost} &= \frac{6,135,000}{10^6} \times 2.21 \\ &= \$13.55/\text{BB1} \end{aligned}$$

d) Distillate Fuel Oil Specific Gravity

$$\begin{aligned} \text{S.G.} &= \frac{141.5}{131.5 + 26} \\ &= 0.898 \end{aligned}$$

e) Distillate Fuel Oil Heat Content

$$\begin{aligned} \text{Heat Content} &= 0.898 (8.33) (42) (19,200) \\ &= 6,042,200 \text{ BTU/BB1} \end{aligned}$$

Residual Fuel Oil Cost

$$\begin{aligned} \text{Cost} &= \frac{6,042,200}{10^6} \times 3.00 \\ &= \$18.13/\text{BB1} \end{aligned}$$

11. Annual Costs

a) Oil Consumption (Residual)

Basis: 150,000 M BTU/hr.

Unit Cost \$2.410/BB1

$$\begin{aligned}\text{BB1/hr} &= 150,000,000 / 6.135 \times 10^6 \\ &= 24.45 \text{ BB1/hr.}\end{aligned}$$

b) Oil Consumption (Distillate)

Basis: 15,000 M BTU/hr.

$$\begin{aligned}\text{BB1/hr.} &= 15,000,000 / 6.0422 \times 10^6 \\ &= 2.48 \text{ BB1/hr.}\end{aligned}$$

c) Incremental Cost

Basis Kuwait Resid, 0.1 Wt. % S

$$\begin{aligned}\text{Cost} &= 24.45 \times 24 \times 330 \times 3.51 \\ &= 679690/\text{yr.}\end{aligned}$$

d) Annual Cost/M BTU/hr.

$$\begin{aligned}\text{Cost} &= 679690 / 150 \times 10^3 \\ &= \$4.53/\text{M BTU/hr.}\end{aligned}$$

e) Cost/KJ/Sec.

Conversion M BTU/hr. $\times$ 0.293 = KJ/Sec.

$$\begin{aligned}\text{Cost} &= 4.53 / 0.293 \\ &= \$15.46/\text{KJ/Sec.}\end{aligned}$$

12. Cost Impacts

Basis: Residual Fuel Oil Cost \$13.55/BB1

a) % Increase over Uncontrolled

$$\begin{aligned}\% &= \frac{3.51}{13.55} \times 100 \\ &= 25.90\%\end{aligned}$$

b) % Increase over S.I.P. Controlled

Basis: S.I.P. Control Cost \$1.80/BB1

$$\% = \frac{13.55 + 3.51}{13.55 + 1.80} - 1 \times 100$$

$$= 11.14\%$$

13. Cost Effectiveness

Basis: 277.7 Long Ton/Day Sulfur

3.51/BB1 Oil

$$a) \text{ C.E. } = \frac{3.51 (50,000)}{277.7 (2240)}$$

$$b) \text{ C.E. } = 0.28 (2.2)$$

$$= \$0.62/\text{KG S Removed}$$

SECTION 5

ENERGY IMPACT OF BEST EMISSION CONTROL SYSTEM FOR CLEAN OIL

5.1 INTRODUCTION

Based upon the rating factors developed in Section 3, hydrodesulfurization was selected as the best system for emission reduction for clean oil technology. To allow for a complete energy impact assessment, a brief description of how and where energy is used in the fuel oil hydrodesulfurization process (HDS) overall is presented here. The description is applicable to both distillate and residual fuel oil, since the HDS processes are similar for both oils.

A small energy debit, which must be assessed against the HDS process is the reduced calorific value of the lighter product resulting from the desulfurization process. This results from a hydrocracking reaction which occurs to a limited extent along with the HDS reaction and which breaks down the heavier hydrocarbons yielding a lighter product of lower calorific value (on a volume basis) than the feed. The normal caloric reduction from HDS usually amounts to about 1% of the nominal 6.15 MMBtu/barrel value. Thus, a greater volume of desulfurized fuel oil is necessary to produce the required heat release in the boiler. However, slight boiler atomizing nozzle modifications can easily compensate for this minor caloric reduction so that there is no noticeable boiler derating as a result of burning the desulfurized fuel oil. No definitive assessment is made in this section of the energy impact of this debit.

The HDS process has not been considered on a stand-alone basis for the energy impact assessment, since auxiliary processes are required to dispose of process by-products. These auxiliary processes include a hydrogen sulfide absorption unit (circulating amine type), sulfur recovery with tail-gas scrubbing (Claus type with reduction system and tail-gas reheat), a sour water stripper (steam stripping), and a hydrogen plant.

HDS Process

The process utilizes a catalytic reaction of oil feed and hydrogen at high temperature and pressure in one or more reactor vessels and hence requires shaft energy to pump liquid and compress hydrogen to reaction pressure. Fossil fuel is required in a preheat furnace to heat the reactants to reaction temperature, while shaft power and cooling water are required by air coolers and water coolers, respectively, to cool the reaction products.

Separation of the reaction products is achieved in both flash drums and fractionation tower, the latter requiring shaft energy to pump feedstream, reflux, and products and shaft energy and/or cooling water to condense overhead products. Low-pressure (LP) steam is used for stripping products in this fractionation tower. This steam is condensed with overhead tower products, separated and routed to the sour water stripper.

H₂S Absorption Process

A circulating amine process is usually used to remove the H₂S produced in the catalytic reaction from both the reaction products and the recycled H₂ returning to the reactor(s). Shaft energy is required to pump the amine between absorption and stripping towers and provide reflux at the latter, while shaft power and/or cooling water provides condensation of stripping steam and cooling of the regenerated amine stream. High-pressure (HP) steam is used to reboil the stripping tower and provide stripping vapors.

Sulfur Recovery and Tail-Gas Scrubbing

Part of the H₂S recovered from the circulating amine is combusted with air to form SO₂ in a combined furnace-waste heat boiler requiring shaft energy to compress air for combustion and pump water to the boiler and producing steam for an energy credit. The H₂S-SO₂ mixture is then reacted over a series of three converters with fixed catalyst beds; sulfur formed in the reactors is condensed in water-cooled condensers. The mixture is then reheated with hot reaction

gases. Tail-gas from the third condensor is combined with combustion products of fossil fuel and compressed air to provide reheat and reducing gas before entering a further reactor to reduce the remaining SO_2 back to H_2S before cooling and absorption in a circulating solution such as used in the Shell Claus Off-Gas Treating Process (SCOT).⁽¹⁾ This process requires shaft energy for pumping the circulating solution and LP steam for regenerating this solution. Sour waste water is released in the cooling process and is sent to the sour water stripper. Fossil fuel is required to incinerate the absorber off-gas before release to the atmosphere.

Sour Water Stripping

Sour water containing H_2S from either the HDS fractionation tower or SCOT process is stripped with LP steam in a stripping tower prior to release to the plant effluent treatment system.

5.2 ENERGY IMPACT OF CONTROLS FOR OIL-FIRED BOILERS

New Facilities

Table 5-1 included in this section provides a detailed listing of the forms of energy utilized in the HDS and auxiliary processes at the various control levels specified viz. SIP, Moderate, Intermediate, and Stringent.

An example calculation for medium sulfur residual-stringent level of control is shown in the Appendix of this section.

Energy vs. Level-of-Control

Low-capacity steam boilers of the fire-tube and Scotch types use distillate fuel oil (i.e., #2) which is presently limited by ASTM specification⁽¹¹⁾ at 0.5% W/W sulfur. This represents an Intermediate level-of-control and is presently used for about 10% of the #2 oil nationwide requirements. The Stringent level-of-control of 0.10 lbs. SO_2 per MM Btu/hr., which represents approximately 0.10% W/W sulfur fuel oil, necessitates a deeper level of desulfurization which requires a lower catalyst space velocity, increased H_2 consumption, and higher temperature levels in the catalyst bed. The plot of energy

TABLE 5-1. ENERGY CONSUMPTION FOR SO₂ CONTROL TECHNIQUES FOR OIL-FIRED BOILERS

System		Energy Consumption					% Change in ^b . Energy Use Over SIP Controlled Boiler	
Standard Boiler	Type	Type & Level of Control	Control Efficiency %	Energy Types	Energy Consumed by Control Device			
Heat Input MW (MBtu/hr)					SI	English	% Increase ^a . in Energy Use Over Uncon- trolled Boiler	
44 (150,000)	Firetube	Desulfurized Distillate Fuel Oil	SIP Moderate Intermediate Stringent	0 0 40 80	Fossil Fuel Fossil Fuel Fossil Fuel Fossil Fuel	325 MJ/m ³ 372 MJ/m ³	- - 49 MBtu/bbl 56 MBtu/bbl	- - 0.8 1.0
		SIP Moderate Intermediate Stringent	0 0 40 80	Electrical Electrical Electrical Electrical	25 MJ/m ³ 32 MJ/m ³	- - 1.1 Kwh/bbl 1.4 Kwh/bbl	- - 0.06 0.08	
		SIP Moderate Intermediate Stringent	0 0 40 80	HP Steam HP Steam HP Steam HP Steam	-21 Kg/m ³ 6.9 Kg/m ³	- - -7.2 lb/bbl 2.4 lb/bbl	- - -0.11 0.04	
		SIP Moderate Intermediate Stringent	0 0 40 80	LP Steam LP Steam LP Steam LP Steam	15 Kg/m ³ 15 Kb/m ³	- - 5.4 lb/bbl 5.4 lb/bbl	- - 0.09 0.09	

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TABLE 5-1. ENERGY CONSUMPTION FOR SO₂ CONTROL TECHNIQUES FOR OIL-FIRED BOILERS (cont'd.)

System		Energy Consumption				Energy types	Control Efficiency %	Type & Level of Control	Standard Boiler Heat Input MW (MBtu/hr)	Type	Watertube	44 (150,000)					
		Energy Consumed by Control Device		% Increase ^a . in Energy Use Over Uncon- trolled Boiler	% Change in ^b . Energy Use Over SIP Controlled Boiler												
		SI	English														
		Desulfurized Residual Fuel Oil		Fossil Fuel	537 ^d MJ/m ³	81 MBtu/bbl	1.3	-									
				Fossil Fuel	597 MJ/m ³	90 MBtu/bbl	1.5	0.1									
		Moderate		Fossil Fuel	630 MJ/m ³	95 MBtu/bbl	1.6	0.2									
		Intermediate		Fossil Fuel	630 ^d MJ/m ³	95 MBtu/bbl	1.6	0.2									
		Stringent															
		-High Sulfur Residuals SIP															

TABLE 5-1. ENERGY CONSUMPTION FOR SO₂ CONTROL TECHNIQUES FOR OIL-FIRED BOILERS (cont'd.)

System		Energy Consumption				% Change in ^b Energy Use Over SIP Controlled Boiler
Standard Boiler	Type	Type & Level of Control	Control Efficiency %	Energy Types	Energy Consumed by Control Device	
Heat Input MW (MBtu/hr)					SI English	
44 (150,000)	Watertube	Desulfurized Residual Fuel Oil				
		-High Sulfur Residuals SIP Moderate Intermediate Stringent	64	Electrical	145 ^d MJ/m ³	0.4
			76	Electrical	181 MJ/m ³	0.5
			94	Electrical	213 MJ/m ³	0.5
			98	Electrical	222 ^d MJ/m ³	0.6
		-Medium Sulfur Residuals SIP Moderate Intermediate Stringent	59	Electrical	120 ^d MJ/m ³	0.3
			75	Electrical	156 MJ/m ³	0.4
			93	Electrical	197 MJ/m ³	0.5
			96	Electrical	208 MJ/m ³	0.5
		-Low Sulfur Residuals SIP Moderate Intermediate Stringent	37	Electrical	61 ^d MJ/m ³	0.1
			75	Electrical	129 MJ/m ³	0.3
			88	Electrical	154 MJ/m ³	0.4
			96	Electrical	168 ^d MJ/m ³	0.4

TABLE 5-1. ENERGY CONSUMPTION FOR SO₂ CONTROL TECHNIQUES FOR OIL-FIRED BOILERS (cont'd.)

System		Energy Consumption					% Change in Energy Use Over SIP Controlled Boiler
Standard Boiler	Type	Type & Level of Control	Control Efficiency %	Energy Types	Energy Consumed by Control Device		
					SI	English	
Heat Input MW (MBtu/hr)							
44 (150,000)	Watertube	Desulfurized Residual Fuel Oil					
		-High Sulfur Residuals SIP	64	HP Steam ^e	9 ^d KG/m ³	3 LB/BBL	-
		Moderate	76	HP Steam	11 ^d KG/m ³	4 LB/BBL	0.01
		Intermediate	94	HP Steam	17 ^d KG/m ³	6 LB/BBL	0.04
		Stringent	98	HP Steam	17 ^d KG/m ³	6 LB/BBL	0.05
		-Medium Sulfur Residuals SIP	59	HP Steam	3 ^d KG/m ³	1 LB/BBL	-
		Moderate	75	HP Steam	6 KG/m ³	2 LB/BBL	0.01
		Intermediate	93	HP Steam	0 KG/m ³	0 LB/BBL	0
		Stringent	96	HP Steam	14 KG/m ³	5 LB/BBL	0.06
		-Low Sulfur Residuals SIP	37	HP Steam	3 ^d KG/m ³	1 LB/BBL	-
		Moderate	75	HP Steam	3 ^d KG/m ³	1 LB/BBL	0
		Intermediate	88	HP Steam	6 ^d KG/m ³	2 LB/BBL	0.01
		Stringent	96	HP Steam	6 ^d KG/m ³	2 LB/BBL	0.01

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TABLE 5-1. ENERGY CONSUMPTION FOR SO₂ CONTROL TECHNIQUES FOR OIL-FIRED BOILERS (cont'd.)

System		Energy Consumption				% Change in ^{b.} Energy Use Over SIP Controlled Boiler
Standard Boiler	Type	Type & Level of Control	Control Efficiency %	Energy Types	Energy Consumed by Control Device	
Heat Input MW (MBtu/hr)					SI	English
44 (150,000)	Watertube	Desulfurized Residual Fuel Oil				
		-High Sulfur Residuals SIP	64	LP Steam ^f	108 ^d KG/m ³	38 LB/BBL
		Moderate	76	LP Steam	143 KG/m ³	50 LB/BBL
		Intermediate	94	LP Steam	217 KG/m ³	76 LB/BBL
		Stringent	98	LP Steam	240 ^d KG/m ³	84 LB/BBL
						0.6 0.8 1.2 1.3
		-Medium Sulfur Residuals SIP	59	LP Steam	94 ^d KG/m ³	33 LB/BBL
		Moderate	75	LP Steam	131 KG/m ³	46 LB/BBL
		Intermediate	93	LP Steam	177 KG/m ³	62 LB/BBL
		Stringent	96	LP Steam	197 KG/m ³	69 LB/BBL
						0.5 0.7 0.9 1.0
		-Low Sulfur Residuals SIP	37	LP Steam	37 ^d KG/m ³	13 LB/BBL
		Moderate	75	LP Steam	86 KG/m ³	30 LB/BBL
		Intermediate	88	LP Steam	120 KG/m ³	42 LB/BBL
		Stringent	96	LP Steam	140 ^d KG/m ³	49 LB/BBL
						0.2 0.5 0.6 0.7

- a. Energy consumed by device, MW ÷ standard Boiler Heat Input, MW x 100 (%)
- b. Moderate, Intermediate, Stringent, energy consumed by control device, MW - SIP energy consumed, MW ÷ standard Boiler heat input, MW + SIP energy consumed, MW x 100 (%)
- c. High Sulfur Residuals - 4+% W/W S
Medium Sulfur Residuals - 3.4% W/W S
Low Sulfur Residuals - 0-3% W/W S
- d. Denotes estimated figures
- e. 87 KPa, 400°C (600 psig, 750°F) steam
- f. 7 KPa, Satd. (50 psig)

consumption versus level-of-control curve is shown in Figure 5-1.

Those utilities related to the HDS process (i.e., fossil fuel and electrical energy) show a predictable increase in consumption with increased severity of desulfurization, while the utilities related to the HDS auxiliary processes (i.e., high- and low-pressure steam) do not follow a logical consumption pattern but rather a change in data source and thus do not provide meaningful information.

With only two data points for each form of energy, it is not possible to locate an optimum point for level-of-control, since the increased SO_2 removal takes progressively more energy to achieve.

The plot of energy consumption versus level-of-control curve for three levels of sulfur content in residual fuel oil is shown in Figures 5-2 through 5-5. Each plot reflects SIP, Moderate, Intermediate, and Stringent level-of-control points and shows a distinct "knee" between Moderate and Intermediate levels for all sulfur content fuel oils, indicating an increased rate of energy consumption between these points.

From these plots, it is not possible to locate an optimum point for an Intermediate level-of-control between Moderate and Stringent levels without developing further data points, the data for which were not available in the public literature.

Each of the energy consumption plots reflects a higher consumption for high-sulfur content residuals than for medium or low and results from the increased amount of sulfur or sulfur by-products produced which requires additional energy consumption both in the HDS unit and the auxiliary processes serving the HDS unit.

Energy Use in Fuel Oil Desulfurization

HDS Process--

Fuel-fired process heaters required to elevate the temperature of the oil feed and H_2 before reaction over catalyst are the largest users of energy in

Figure 5-1
Energy Consumption vs. Level-of-Control
for Distillate Fuel Oil

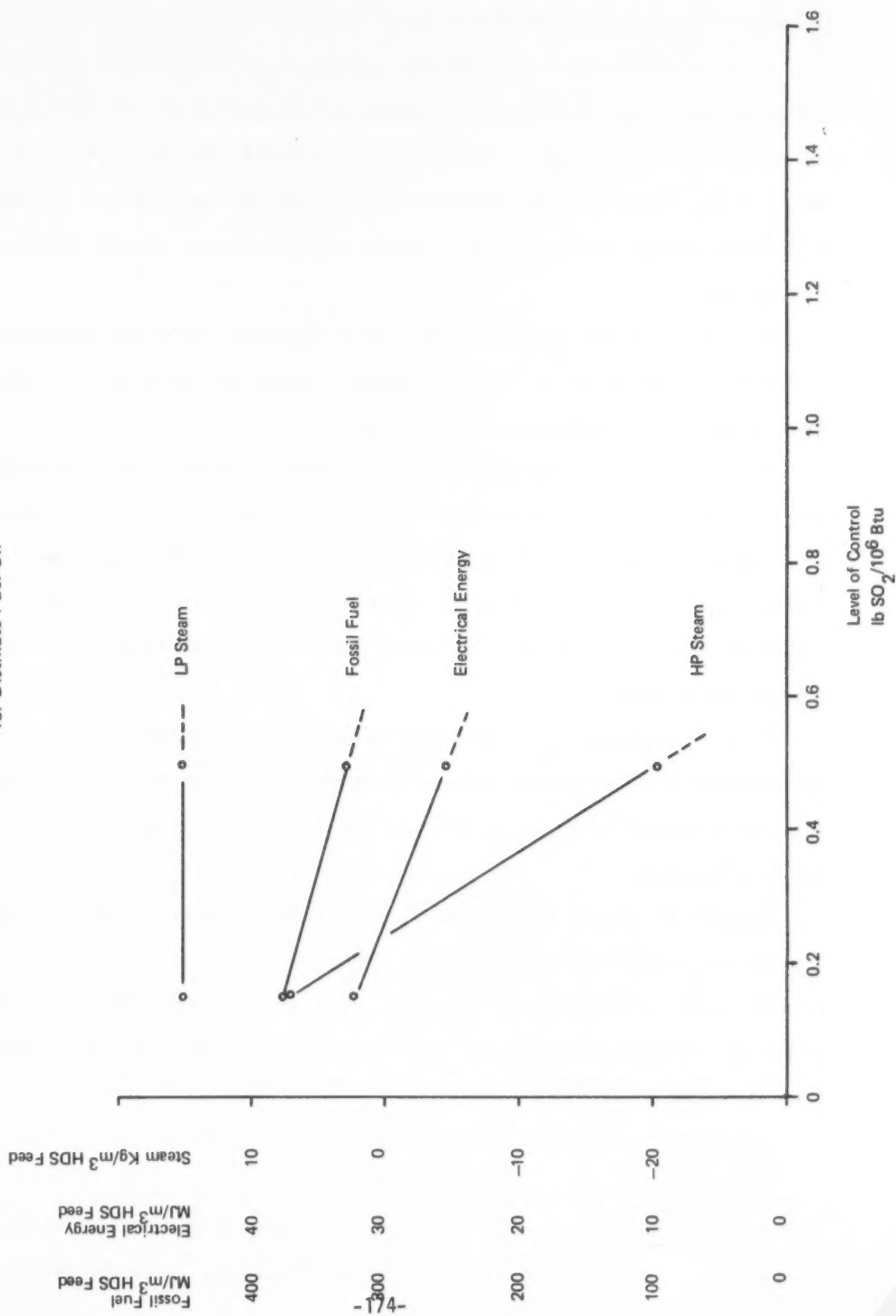


Figure 5-2
Fossil Fuel Energy Consumption
of High/Medium/Low Sulfur Residual
Fuel Oils vs. Level-of-Control

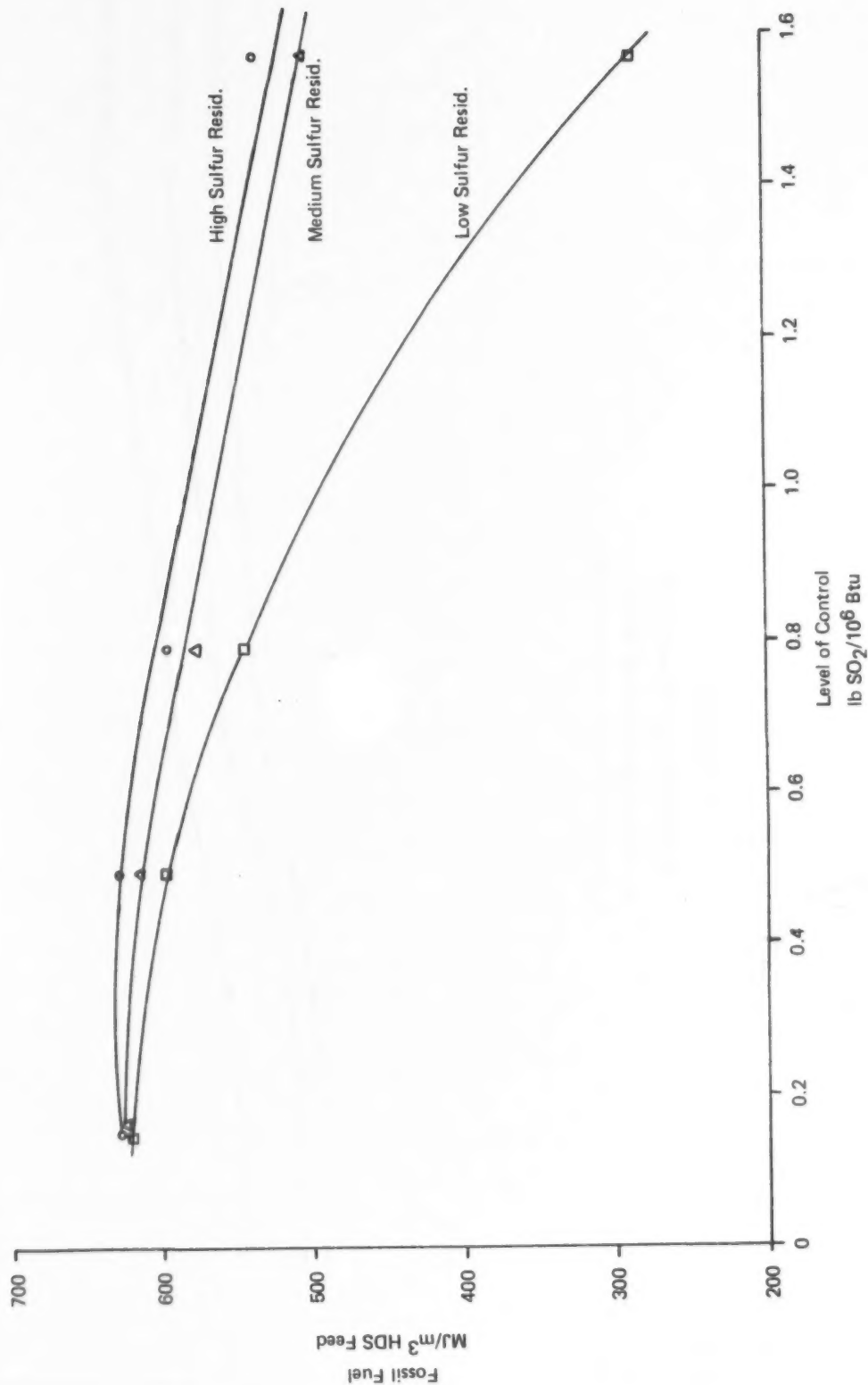


Figure 5-3
Electrical Energy Consumption
of High/Medium/Low Sulfur
Residual Fuel Oils vs. Level-of-Control

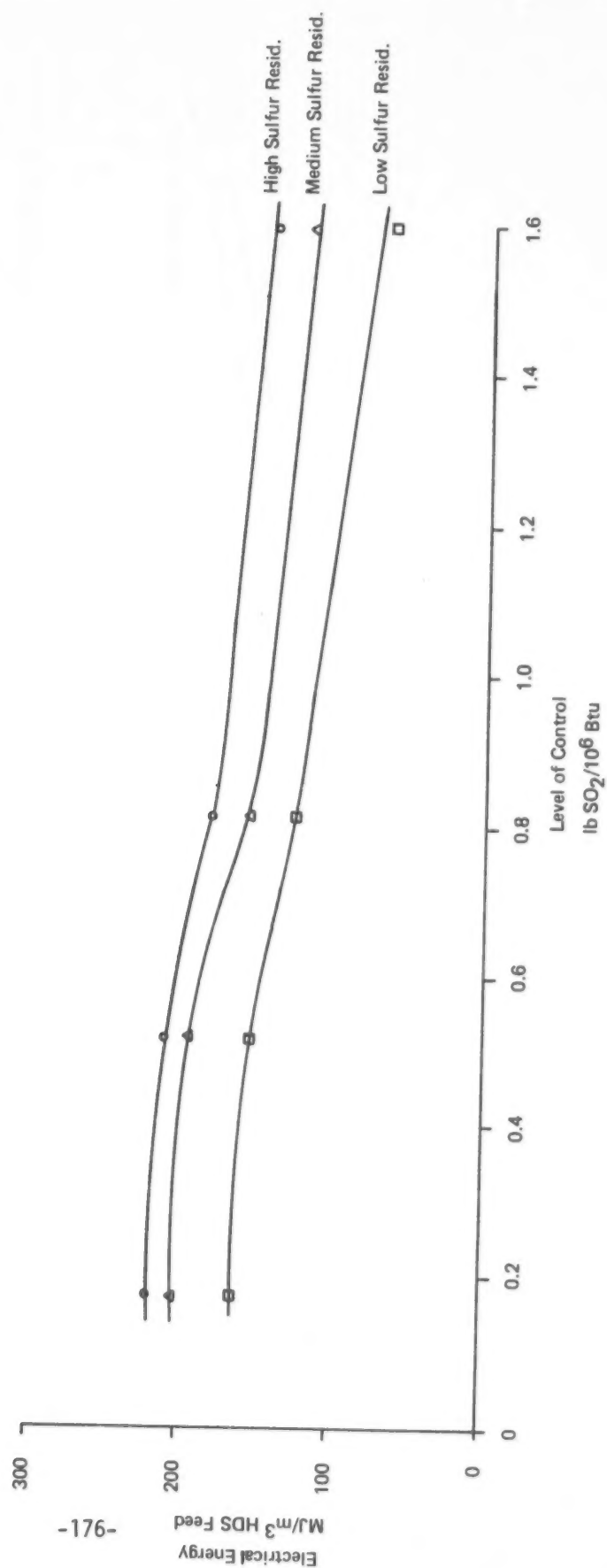


Figure 5-4
 HP Steam Consumption
 of High/Medium/Low Sulfur
 Residual Fuel Oils vs. Level-of-Control

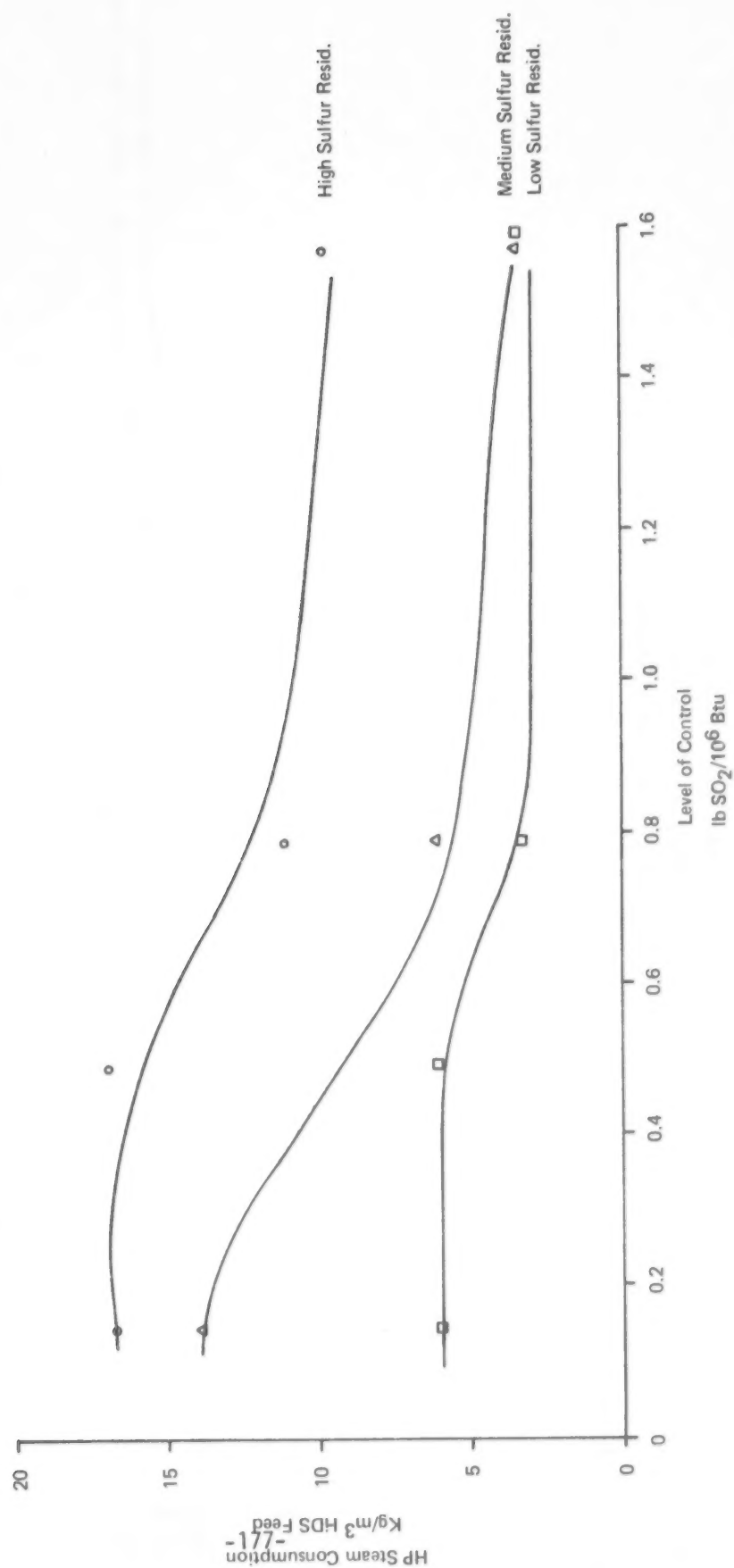
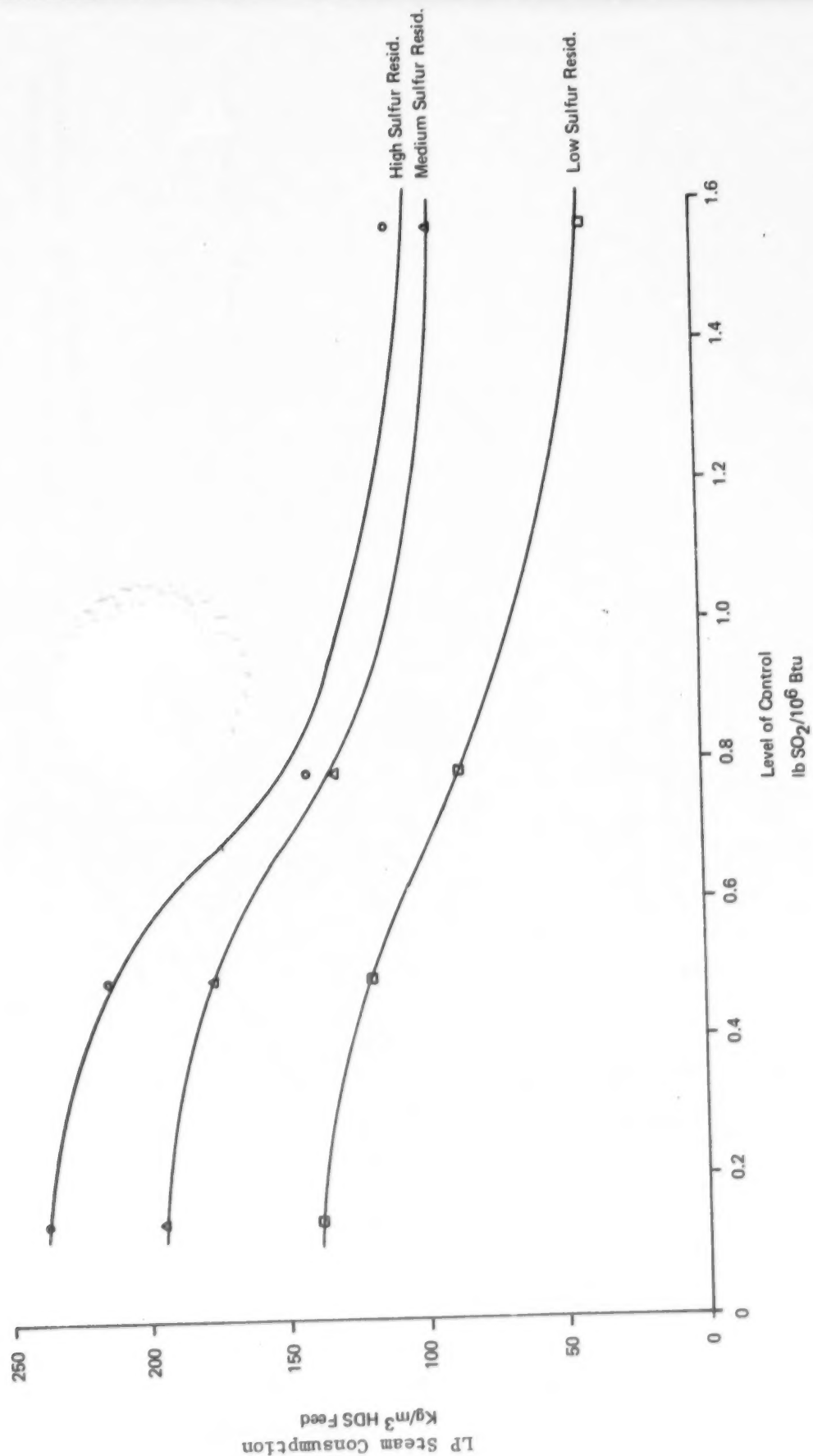


Figure 5-5

LP Steam Consumption of
High/Medium/Low Sulfur
Residual Fuel Oil vs. Level-of-Control



the HDS process. The fuel used depends on the refinery product balance and can range from fuel gas to a residual fuel, the latter being a captive use for less desirable by-products of the refining process. Residual fuel oil is the most common type of fuel in this duty. Fuel gas is universally used as a source for pilot gas, the usage being small.

Motor-driven high-pressure compressors for compressing both fresh and recycle H_2 before mixing with oil feed are large users of power in this process. Standby machines are usually provided with steam turbine drive as described below.

Air-coolers are often used to condense and cool both reactor products and fractionation tower overheads, and the motor-driven fans represent a major user of power.

Motor-driven feed pumps are used to transfer oil feed to the high-reaction pressure condition necessary for hydrodesulfurization and represent a major use of power. Other pump duties such as fractionation tower feed and reflux, product pumping, are less severe and use relatively less power.

Lighting, instrumentation, and line tracing are other small users of power.

High-pressure (600 psi) steam is used to provide a steam turbine drive for standby critical equipment such as the H_2 compressors and oil feed pump and are operated normally only when required by the refinery steam balance.

Low-pressure (50 psi) steam is used mainly as stripping steam in the product fractionation tower which represents a major use of steam.

Steam heating coils and tracing to maintain heavy oils above their pour point represent a minor use of steam.

Amine Process--

Motor-driven pumps are used to circulate the H_2S -absorbing solution of amine between absorption and stripping towers, as well as providing reflux

for the stripping tower. Anti-foam injection pumps and amine make-up pumps also draw a small quantity of power.

Air-coolers used to condense stripping tower reflux and cool lean amine utilize motor-driven fans and are major users of power.

Lighting and instrumentation are minor users of power in this process.

Low-pressure (50 psi) steam is used as a reboiler heating medium on the stripping tower and represents a major use of steam. Steam heating coils and tracing used to prevent the amine from freezing are small users of steam.

Sulfur Plant and Tail-Gas Scrubbing--

A fuel-fired line burner is used in the Tail Gas Scrubbing unit to provide reducing gases to reduce SO_2 back to H_2S in the Reduction type of Tail-Gas unit used as a basis for this discussion. A fuel-fired incinerator is used after the Tail-Gas Scrubbing unit to convert all traces of H_2S back to SO_2 and provide a stack exit temperature high enough to provide stack-gas bouyancy upon release to the atmosphere. The incinerator represents the major user of fuel which is a refinery fuel gas rather than fuel oil type.

Motor-driven air compressors are necessary to provide combustion air for the Sulfur Plant Furnace reaction of H_2S to SO_2 before passing the gases over catalyst beds and represent the major user of power in this process.

Motor-driven pumps are used to load liquid sulfur into tank cars and circulate the absorbing solution in the Tail Gas Reduction process.

Air-coolers used in the Tail Gas Reduction process to reduce process gas temperature prior to absorption in the circulating amine utilize motor-driven fans. Lighting and instrumentation are minor users of power in this process.

High-pressure (600 psi) steam is produced in the combination furnace-waste heat boiler in the Sulfur Plant and results from the highly-exothermic reaction of H_2S to SO_2 in the furnace. This steam is not used in the process and is thus utilized elsewhere in the refinery steam balance.

Low-pressure (50 psi) steam is produced in the sulfur condensers downstream of each catalyst bed of the Sulfur Plant and condenses liquid sulfur from the reaction product gases. Only a small amount of this steam is used in the Sulfur Plant for heating coils and jacketted piping, the balance being exported to the refinery steam balance.

Low-pressure (50 psi) steam is also utilized downstream of the Reduction type of Tail-Gas Scrubbing Unit catalyst bed and as reboiler heating medium in a circulating amine stripping tower shared with other amine absorbers on the refinery.

Sour Water Stripper--

Low-pressure (50 psi) steam is used as both a heating and stripping medium in the sour water stripping tower to remove H_2S and NH_3 from contaminated waste water before releasing the water to the refinery effluent treating system.

Hydrogen Plant--

Most refinery hydrogen requirements are produced in catalytic reforming units; the advent of desulfurization requirements has meant the installation of a hydrogen facility. Within the context of previous discussion in Section 4, the energy impact of such a separate hydrogen plant will be examined. A typical hydrogen plant consists of a sulfur guard unit, reformer furnace, CO shift reactor, CO_2 removal unit, methanation unit, and make-up gas compressor. The most common feedstock for hydrogen production is a hydrocarbon source, usually naphtha, from the refinery complex. The naphtha is vaporized, mixed with steam, and passed over a nickel catalyst at temperatures of 1200-1800°F.

The energy requirements of the hydrogen plant concentrate on the delivery of the naphtha and steam input to the reformer. To achieve 1200-1800°F in the reformer and high pressure, about 3000 lb/hr high-pressure steam (500 psig, 750°F) and 5-7,000 lb/hr medium-pressure (450 psig, saturated) steam have to be supplied for a 50 MSLFD H_2 plant. Some medium-pressure steam is produced during

methanation, which can be used elsewhere or recycled prior to reforming to serve as an overall credit. This level of steam production can easily utilize 1400-1500 gal/MCF cooling water and 4-6 gal/MCF boiler feed water.¹²

Multi-stage compression of hydrogen to be supplied to the HDS unit represents a substantial energy outlay. Depending upon the pressure requirement of the HDS, the hydrogen compressor output can range between 150 psig and 330 psig. At a normal compression ratio of 2.0 (outlet/inlet pressure), about 45 bhp is required for rotary or reciprocating compressors. This gives a range of power required between 0.02-0.08 hp-hr/barrel processed solely for the hydrogen plant, depending upon the compression level.

Electric power consumption for a hydrogen plant ranges between 1.4 KWH/MSCF H_2 and 1.6 KWH/MSCF H_2 , which means 1.4-1.6 KWH/barrel for the average HDS hydrogen consumption of 1000 CF/barrel processed.¹³

The largest energy impact from hydrogen production comes from the natural gas fuel and process feed natural gas consumed during steam reforming. Process feed gas utilizes about 260 SCF natural gas/MSCF H_2 , and the natural gas fuel requirements are about 415 SCF natural gas/MSCF H_2 (415 MBtu/MSCF H_2).

Energy Conservation Options

A significant reduction in fuel use is achieved where control of excess air used in the heater is practiced by means of stack gas monitoring using analytical instrumentation either on an intermittent or continuous basis. The accompanying reduction in combustion air fan power also results from this excess air control. The provision of combustion air preheating, additional convection zone heat transfer surface, as well as soot blowing facilities, would also improve furnace efficiency.

A reduction in energy use by improved maintenance practices results from higher-efficiency operation of furnace burners, furnace fans, air-cooler fans, gas compressors, liquid pumps by cleaning burner tips, and fluid filters

throughout the unit. These operations are usually already performed on a regular basis.

Optional maintenance practices imply a trade-off of energy saved versus the cost of implementing maintenance procedures and is a difficult topic to categorize. Generally, regular preventative maintenance programs will perform the necessary energy-saving activities at a cost, while breakdown maintenance programs only replace items no longer serviceable and are not the most energy-efficient method. The choice of a maintenance program is very subjective, as detailed payout studies are not available, since industry is not uniform in the choice of which maintenance program is superior.

Stack gas heat recovery is not applicable to the fuel pretreatment process discussed here.

Less energy intensive process is not applicable, since an HDS process is the subject for discussion.

Fuel switching is not applicable, since both distillate and residual fuel oil have been selected for discussion.

A considerable amount of heat previously released to the atmosphere via air or water-condensers/coolers is now being recovered in exchange with process- or steam-raising duties. In addition, closer temperature approaches than previously used are now being designed.

As air-coolers are designed for the hottest part of the year, considerable savings in power are possible where the fan pitch is changed to reduce air rate by means of variable-pitch controllers during cooler weather.

High-pressure streams that are depressurized via a hydraulic turbine recover part of the energy necessary to achieve these high pressures and are usually coupled with a pump and motor-driver to reduce the overall power consumption of the pump.

Energy Conservation Savings

Specific estimates of energy savings resulting from a conservation program depend on the standard of operation before the program is instituted which varies between various refineries, but general savings found are available. A recent survey of 12 furnaces revamped for energy conservation shows average increase in efficiency from 76% to 88%⁽¹³⁾, while using preheated combustion air from air-coolers could save 2% of the energy.⁽¹⁴⁾

Variable-pitch fans or multiple-fan units can lead to use of less than half the design power consumption required by most air-coolers.⁽¹⁵⁾ General savings for improved maintenance and increased heat exchange are very specific to the installation, and no general figures are presented here.

Energy Conservation Drawbacks

The overriding drawback to all energy conservation measures is the increased cost associated with additional equipment or hardware necessary and the payout time to realize a cost saving. The price and availability of fuel is the economic pointer in the selection of conservation measures, and most refiners will use an expected payout time of 2-5 years or a discounted cash flow of 15% in the choice of possible options.

Other drawbacks encountered include temperature level of waste heat which cannot be reused directly in the process, but may be utilized where a heat pump is supplied to boost temperature levels of heat available.

Modified and Reconstructed Facilities

Where provision has not been made at the design stage to upgrade the extent of sulfur removal in the HDS process, the retrofit of an existing process is extremely costly and often not considered economic in the refining industry. Where provision for future upgrading is made, large equipment and pipework are usually installed during initial construction, making the retrofit a relatively simple procedure. The comments for New Facilities would then apply in this section.

5.3 SUMMARY

The production of low-sulfur distillate and residual fuel oils by pre-combustion treatment methods, such as the hydrodesulfurization (HDS) process discussed in detail here, will have the advantage of scale from the energy impact point of view, since the HDS process is centralized; and, advantage can be taken of the large scale of utility consumption/production. The HDS process, however, is a high-pressure, high-temperature process and, consequently, the energy consumption to operate the equipment is extensive. The use of HDS as an SO₂ control technology on industrial boilers results in the expenditure of 2-4% of the energy generated by the boilers. When the energy consumption of the hydrogen plant is factored into a total desulfurization energy consumed, the percentage of energy used increases substantially. The following table shows the desulfurization energy expenditure as a percentage of total boiler energy generated for the various sulfur control levels:

<u>Sulfur in Fuel Oil</u>	<u>Energy Consumed As A Percentage of Energy Generated</u>
1.6% S	4.5%
0.8% S	5.6%
0.3% S	8.6%
0.1% S	10.8%

Table 5-2 shows energy consumption for the HDS and hydrogen plant utilities as a function of desulfurization levels. It is apparent that, to achieve low sulfur levels (0.3% S or 0.1% S) necessary for industrial boiler combustion without controls, substantial energy inputs are needed as the degree of desulfurization increases.

TABLE 5-2. ENERGY CONSUMPTION FOR SULFUR LEVEL-OF-CONTROLS IN RESIDUAL OIL

Crude Class	Utility	Sulfur in Fuel Oil			
		1.6%	0.8%	0.3%	0.1%
Low Sulfur <3% S	Power	2.9	6.4	8.2	8.7
	Steam	12.8	28.3	44.4	48.6
	Fuel	107.7	262.9	360.0	398.7
	Cooling Water	.31	.63	1.1	1.2
Med. Sulfur 3-4% S	Power	5.8	7.7	10.0	10.5
	Steam	31.0	43.8	63.8	71.2
	Fuel	227.5	314.8	364.2	393.1
	Cooling Water	.65	.94	1.2	1.2
High Sulfur >4% S	Power	7.0	8.9	10.7	11.0
	Steam	37.4	49.2	79.6	84.4
	Fuel	257.4	334.0	382.2	403.1
	Cooling Water	.75	.99	1.15	1.23

NOTE: Utility Units
 Power in KWH/Bbl
 Steam in MBtu/Bbl
 Fuel in MBtu/Bbl
 Cooling Water in MGal/Bbl

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APPENDIX

1. Control Efficiency

Stringent level of control = 0.10 lbs. SO_2 per MM BTU
= 0.10% W/W sulfur

Typical medium sulfur content residual

= 3.8% W/W at 16.6^C API (Kuwait)

Typical HDS 375^{OF} Product for Stringent Level

= 97.4% yield with 0.1% W/W sulfur at 25.0^O API

Control Efficiency = $\frac{\text{sulfur removed per barrel} \times 100}{\text{total sulfur per barrel}}$

$$= \frac{(0.038 \times 0.96 \times 42 \times 8.33 - 0.001 \times 0.90 \times 42 \times 8.33 \times 0.974)}{0.038 \times 0.96 \times 42 \times 8.33}$$

$$= \frac{(12.76 - 0.31)}{12.76} \times 100$$

= 98%

2. Energy Consumed by Control Device

A. HDS Process Energy Consumption per Barrel Feed

Fuel - 84 M BTU

Power - 8.4 KWh

600# Steam - 29 lbs.

50# Steam - 52 lbs.

B. Amine Process

$$\text{H}_2\text{S absorbed per barrel HDS feed} = (12.76 - 0.31) \times \frac{34}{32}$$

$$= 13.23 \text{ lbs.}$$

Energy Consumption:

Power = 0.025 KWh per lb. H_2S absorbed

= 0.33 KWh/bbl HDS feed

50# Steam = 2 lb. per lb. H_2S absorbed

= 26.5 lbs./bbl HDS feed

C. Sulfur Plant and Tail Gas Scrubbing-Utility Consumption

$$\text{Sulfur plant feed per barrel HDS feed} = 13.23 \times \frac{32}{34 \times 2240}$$

$$= 0.006 \text{ Long Tons}$$

Energy Consumption:

$$\begin{aligned} \text{Fuel} &= 1.78 \text{ MM BTU/Long Ton} \\ &= 9.9 \text{ M BTU/bbl HDS feed} \end{aligned}$$

$$\begin{aligned} \text{Power} &= 88.8 \text{ KWh/Long Ton} \\ &= 0.49 \text{ KWh/bbl HDS feed} \end{aligned}$$

$$\begin{aligned} 600\# \text{ Steam} &= 4,320 \text{ lbs/Long Ton produced} \\ &= (24) \text{ lbs/bbl HDS feed} \end{aligned}$$

$$\begin{aligned} 50\# \text{ Steam} &= 1,800 \text{ lbs/Long Ton produced} \\ &= (10) \text{ lbs/bbl HDS feed} \end{aligned}$$

D. Sour Water Stripper

Sour water produced from stripping steam used in
produced fractionation tower (steam rate = 10 lbs/bbl
product rate)

Water treated per barrel HDS feed

$$= \frac{10}{8.33} = 1.2 \text{ gal.}$$

Energy Consumption:

$$\begin{aligned} 50\# \text{ Steam} &= 0.8 \text{ lbs/gal. treated} \\ &= 1.0 \text{ lbs/bbl HDS feed} \end{aligned}$$

Total Energy Consumed per barrel HDS feed

$$\text{Fuel} = 94 \text{ M Btu}$$

$$\text{Power} = 9.2 \text{ KWh}$$

$$600\# \text{ Steam} = 5 \text{ lbs.}$$

$$50\# \text{ Steam} = 69 \text{ lbs.}$$

3. Increase in Energy use over Uncontrolled Boiler-Residual Fuel Oil rate for 150 MM Btu/hr. Boiler = 24.97 bbl/hr. of 25.0⁰ API product
- % Increases:

$$\text{Fuel} = \frac{94 \times 1000 \times 24.97 \times 100}{150,000,000}$$

$$= 1.6\%$$

$$\text{Power} = \frac{9.2 \times 24.97 \times 3412.2 \times 100}{150,000,000}$$

$$= 0.53\%$$

$$600\# \text{ Steam} = \frac{5 \times 24.97 \times 903^* \times 100}{150,000,000}$$

$$= 0.08\%$$

$$50\# \text{ Steam} = \frac{69 \times 24.97 \times 911^{**} \times 100}{150,000,000}$$

$$= 1.0\%$$

4. Change in Energy Use over SIP Controlled Boiler Residual Fuel Oil rate for 150 MM Btu/hr. Boiler = 24.23 bbl/hr at SIP control level
- % Increases:

$$\text{Fuel} = \frac{(94-76) \times 1000 \times 24.97 \times 100}{(150,000,000 + 76 \times 1000 \times 24.23)}$$

$$= 0.3\%$$

$$\text{Power} = \frac{(9.2-5.3) \times 24.97 \times 3412.2 \times 100}{(150,000,000 + 5.3 \times 24.23 \times 3412.2)}$$

$$= 0.2\%$$

$$600\# \text{ Steam} = \frac{(5-1) \times 24.97 \times 903 \times 100}{(150,000,000 + 1 \times 24.23 \times 903)}$$

$$= 0.06\%$$

$$50\# \text{ Steam} = \frac{(69-33) \times 24.97 \times 911 \times 100}{(150,000,000 + 33 \times 24.23 \times 911)}$$

$$= 0.5\%$$

* Enthalpy - 600 psig, 750⁰F steam = 1,378 BTU/lb.
 - 600 psig saturated liquid = 475 BTU/lb.

** Enthalpy - 50 psig, saturated steam = 1,179 BTU/lb.
 50 psig, saturated liquid = 268 BTU/lb.

SECTION 6

ENVIRONMENTAL IMPACT OF DESULFURIZATION TECHNIQUES FOR THE PRODUCTION OF LOW-SULFUR FUEL OIL

6.1 INTRODUCTION

This section deals with the multimedia environmental impacts associated with the production of low-sulfur fuel oil in the petroleum refining industry. Also included are the environmental impacts associated with the use of low-sulfur fuel oils at the industrial boiler site. The basic intent of this section is to identify the major environmental concerns, both beneficial and adverse, at the boiler and at the refinery for air emissions, water emissions, and solid waste emissions.

Fuel Oil Refinery

The fuel oil refinery as a basic processing sequence is defined by a yield of product fuel oil between 40 and 60% of the liquid processed with the bulk of the remainder of the products being gasoline. To identify the major environmental concerns associated with producing a clean fuel, one must first explore the basic fuel oil refinery processing scheme in order to understand the base emissions associated with producing fuel oil. It is not within the scope of this section to describe or define all the basic refinery processing steps, but rather to compare the environmental impacts of burning uncleaned fuels with the combined impacts of oil cleaning at the refinery plus burning cleaned fuels in an industrial boiler. Once the basic waste stream characterization has been made and the pollutants have been identified for the basic refinery producing fuel oil, then the major environmental impacts can be determined for cleaning the fuel oil from a normal high-sulfur concentration down to a concentration which would meet stringent, moderate, or intermediate control requirements. Then, the incremental environmental effects for this clean oil technology can be assessed on a multimedia basis.

Air Emissions

The major air pollution sources for particulates, SO_x , carbon monoxide, and NO_x within a fuel oil refinery are the process heaters and boilers. The heaters and boilers used for these units are directly fired by refinery fuel gas, heavy fuel oil, or coke gas. The major sources of hydrocarbon emissions are general fugitive emissions throughout the refinery. The exact sources are difficult to identify and even harder to quantify.⁽²⁾ Another major source of hydrocarbons are the crude and petroleum products storage tanks. Another primary pollution source is the tail gas from the acid gas treating plant. New methods of controlling emissions can remove up to 99.8% of the hydrogen sulfide originally introduced to the acid gas plant.⁽³⁾ However, due to the relatively large volume of the acid gas stream, the total emission of SO_x to the atmosphere after treating is still very substantial. Another air emission source within the fuel oil refinery may be associated with the incineration of sludge from wastewater treatment processing. If not incinerated, this sludge would then represent a solid waste disposal problem.

Water Emissions

Major sources of contaminated water within the fuel oil refinery are sour water stripper condensate, process water, cooling tower blowdown, and desalter water. Other potential contaminated water sources are oily process area storm water, oily cleaning water, and oily water from a ship's ballast, if the refinery is located near a docking facility. The combined wastewater from these sources is usually treated in a wastewater treating plant. Sanitary wastewater is also generated within the refinery. This water is handled separately from the contaminated water by a segregated wastewater system. The sanitary wastewater, along with treated process wastewater, is retained in a holding pond for a certain period of time before discharge. The wastewater from different sources within the refinery are segregated and treated together in common equipment based on the most cost effective treatment scheme.

Solid Emissions

The major sources of solid wastes within the fuel oil refinery include entrained solids in the crude, silt from surface drainage, silt from water supply, corrosion products from process units and sewer systems, solids from maintenance and cleaning operations, sludge from water treatment facilities, and spent catalysts. With the exception of spent catalysts, the generated solid wastes are usually considered inert and acceptable for landfill. The solids collected in the API separator and wastewater treating facilities represent about 3/4 of the total solid wastes from a fuel oil refinery.⁽⁴⁾ The balance is from spent catalysts from hydrotreating and hydrodesulfurization units and represents an average of the intermittent catalyst regenerations.

Environmental Effects

There are numerous beneficial environmental effects resulting from the combustion of clean fuel at the industrial boiler. Simply stated, the combustion of clean fuel oil at the industrial boiler will result in lower sulfur oxide, NO_x , and particulate emissions, as well as potentially-reduced solid wastes.

Although no two refineries are exactly alike, the environmental impacts presented in this chapter are based upon the production of low-sulfur fuel oil in a fuel oil refinery. Table 6-1 summarizes the multimedia environmental impact at the fuel oil refinery for a base case of producing a residual fuel oil having a sulfur content of 3.0% and a distillate fuel oil having a sulfur content of 0.5%. These emissions would then be representative of a fuel oil refinery which utilizes a processing sequence established to promote the yield of product fuel oil. The fuel oil produced is considered to be approximately 50% by volume of the total liquid product with the remainder of the products being gasoline. The remainder of this chapter will first define the incremental adverse environmental effects of producing varying grades of clean oil at the refinery. Secondly, these incremental adverse effects at the refinery

TABLE 6-1. ENVIRONMENTAL IMPACT OF A FUEL OIL REFINERY
PRODUCING 3.0% S RESIDUAL AND 0.5% S DISTILLATE OILS⁽⁴⁾

Air Emissions		(lb./M BBL Crude Processed)
Particulates		63.2
SO _x		160.0
NO _x		118.3
CO		12.0
Hydrocarbons		740
Water		(lb./M BBL Crude Processed)
Suspended Solids		2.5
Dissolved Solids		92.6
Organic Material		0.5
Solid Wastes		(lb./M BBL Crude Processed)
Catalysts		20
Other*		60

Source: "Environmental Problem Definition for Petroleum Refineries, Synthetic Natural Gas Plants, and Liquefied Natural Gas Plants," Radian Corp., November 1975, EPA-600/2-75-068.

* Includes: (1) entrained solids in the crude; (2) corrosion products; (3) silt from drainage and influent water; (4) maintenance and cleaning solids; and (5) waste water treatment facilities.

will be compared with the beneficial environmental effects of burning clean fuel in an industrial boiler. This impact analysis will then be used to determine the overall environmental benefit of cleaning fuel oil at the refinery followed by combustion of the fuel oil at the boiler.

Present Capability

Current refinery feedstocks permit production of 0.8 wt. % sulfur fuels by indirect means.⁽¹⁾ These processes involve desulfurization of distillate fuels or vacuum gas oil combined with back-blending to produce residual fuel oils of acceptable sulfur content. Sulfur levels below this or higher sulfur crudes will require the installation of direct desulfurization facilities to meet lower sulfur limits. This is valid only for the domestic refiners, however. Offshore refiners are already faced with direct desulfurization of atmospheric residua in order to produce residual fuel oils of adequate quality for some areas in the United States requiring 0.5 wt. % sulfur residual fuel oil or lower.⁽⁶⁾⁽⁷⁾

6.2 AIR POLLUTION

The refinery airborne emissions of major consequence are generated by four types of sources: combustion sources, process units, effluent control systems, and storage facilities. Each of these source categories is discussed below with emphasis on its contribution to the incremental environmental impact of producing low-sulfur residual fuel oils.

Combustion Sources

Direct-fired process heaters and boilers are the major air pollution sources within the refinery. The emissions from each of the many refinery processing units which contain direct-fired heaters are dependent on the unit heating requirement and on the fuel used. Total refinery heating demand is approximately 4.5×10^5 BTU/bbl of fuel oil produced. Specific unit heating demands vary widely, and the specific fuels fired vary from heavy fuel oil to

refinery fuel gas or mixtures thereof. The atmospheric emissions are highest from large duty heaters firing heavy fuel oils.

In order to produce low-sulfur fuel oils, it is necessary to add hydrodesulfurization processing capacity. The additional processing heating requirements include: hydrodesulfurization, amine scrubbing, Claus plant, tail gas treating, sour water stripping, and hydrogen plant. The total heating demand for this processing ranges from 5 to 8×10^3 BTU/bbl of fuel oil depending on the degree of desulfurization.

The environmental impact associated with combustion sources in the refinery's clean oil processing is therefore only 1 to 1.5% greater than the baseline refinery atmospheric emissions from direct-fired heaters presented in Table 6-2. The emission rates of the primary pollutants tabulated in Table 6-2 are for a baseline fuel oil refinery producing 3.0% S residual fuel oil. The sulfur oxide emissions are based on refinery sulfur balances, and the emission quantities for particulate and NO_x were determined based on emission factors.

Process Units

Emissions from the process units would be associated, for example, with the regeneration of spent catalysts in the reformer isomeriser, hydrotreaters, or hydrodesulfurization processes (HDS). The catalyst loses its activity due to the accumulation of carbonaceous deposits and to the deposition of trace metals. As the unit continues to operate, the pressure drop across the bed builds up; and, eventually, the process must be shut down. The catalyst may be regenerated by burning off the carbonaceous material or it may be replaced by new catalyst. With a mild treatment, regeneration may be required at yearly intervals; but, where treatment conditions are severe and with the older-type catalysts, regeneration will be required at more frequent intervals.

Additional HDS capacity for producing low-sulfur fuels may result in some minimal increase in particulate loading. However, this emission loading is

TABLE 6-2. BASELINE FUEL OIL REFINERY ATMOSPHERIC
EMISSIONS (LB/M BBL CRUDE PROCESSED)

<u>Sources</u>	<u>Parti- culates</u>	<u>SO_x</u>	<u>CO</u>	<u>Hydro- carbons</u>	<u>NO_x</u>
Crude Distillation	31	64	5	5	53
Gas Oil Hydrotreater	3	5	1	1	11
Naphtha Hydrotreater	--	--	--	--	2
Heavy Naphtha Hydrotreater	20	41	3	3	34
Propane Deasphalting	5	7	1	1	7
Deasphalted Oil Hydrotreater	--	--	--	1	4
Tail Gas Treating	--	34	--	--	--
Light Ends Recovery	--	--	--	--	--
C ₅ /C ₆ Isomerization	1	3	--	--	2
Storage	--	--	--	119	--
Sludge Incineration	4	6	1	1	5
Miscellaneous Emissions	--	--	--	609	--
Total	64	160	12	740	118

Source: "Environmental Problem Definition for Petroleum Refineries, Synthetic Natural Gas Plants, and Liquefied Natural Gas Plants," Radian Corporation, November 1975, EPA-600/2-75-068.

intermittent and only a minor contributor.

Effluent Control Systems

Emissions from the effluent control systems would be represented by stack gas from the tail gas treating system on the Claus plant. Conversion efficiencies in the Claus plant from 95% to 98% can be attained but will depend on the hydrogen sulfide concentrations in the acid gas feed to the unit, the number of catalytic stages, and the quality of the catalyst used. When processing large volumes of acid gas, however, the total SO_x emission from the Claus unit is large and requires further treatment by tail gas treating unit. Some of the tail gas units available are the Bevon (Union Oil of California), Clean Air (J. F. Pritchard & Co.), I.F.P. process, Shell Claus off-gas treating - SCOT (Shell Development Co.), Sulfrene (SNPA-Lurgi - the R. M. Parsons Co.), and W-L SO_2 recovery (Wellman-Power Gas, Inc.).⁽⁸⁾ All of these units will increase the Claus recovery of the equivalent sulfur in the tail gas to greater than 99.5%. The use of different units is determined by the characteristics of the tail gas, the operating conditions, and the economics of the situation. Because of the high sulfur recovery efficiency realized in the tail gas treating process, the sulfur oxides emissions representative of the production of low-sulfur fuel oils are minimized; and, therefore, the relative adverse environmental impact for sulfur oxides at the refinery is minimal when compared with the direct emission of all sulfur contained in the fuel oil when combustion takes place at the industrial boiler site.

Storage Facilities

Hydrocarbon emissions from the storage of heavy and light fuel oils are negligible when compared with the hydrocarbon emissions from crude and gasoline storage tanks. However, there may be a minor adverse environmental impact resulting from the larger fraction of light ends produced in hydrodesulfurization processing. These processing changes will have a negligible effect on total hydrocarbon emissions from the combined refinery storage facilities.

The storage emissions included in the baseline pollutant profile (Table 6-2) are based on emission factors; however, general fugitive emissions included under miscellaneous sources throughout the refinery are the major source of hydrocarbon emissions.⁽²⁾ With the increasing value of hydrocarbons, more effective systems for controlling storage tank losses are becoming economically feasible.

Overall Environmental Analysis

In Tables 6-3, 6-4, and 6-5, an approximation is given of the relative adverse environmental effects of burning high sulfur residual oil in an industrial boiler or of producing low-sulfur residual fuel oil and burning in the same industrial boiler. The primary air pollutants (SO_x , NO_x , and particulate) emitted by the refinery cleaning processes are identified by the processing sources needed for removing sulfur from the fuel oil. The estimated air emissions at the refinery for these processing requirements are given in units which may be directly compared with the air emissions expected at the industrial boiler firing the same fuel with no environmental controls.

Table 6-3 shows that without hydrodesulfurization (no controls), the emission levels for industrial boiler combustion will lead to a significant deterioration of air quality. Table 6-4 shows that, for moderate hydrodesulfurization producing a 0.8% sulfur fuel oil, the incremental SO_x emissions at the refinery are estimated to be less than 4% of the SO_x emissions at the industrial boiler firing residual fuel oil containing 0.8% wt. sulfur. Similarly, Table 6-5 shows the relative air emissions for producing 0.1% sulfur residual fuel oil and for burning this fuel in an industrial boiler.

In summary, there is a significant overall improvement in air quality as a result of burning lower sulfur residual oil fuel. The beneficial effect of lower sulfur fuel is summarized in Table 6-6.

TABLE 6-3. ESTIMATED AIR EMISSIONS, 3.0% S FUEL OIL (NO CONTROL LEVEL)
LB/10⁶ BTU FUEL OIL

<u>Emission Sources</u>	<u>SO_x</u> <u>(lb/10⁶ Btu Fuel Oil)</u>	<u>NO_x</u> <u>(lb/10⁶ Btu Fuel Oil)</u>	<u>Particulate</u> <u>(lb/10⁶ Btu Fuel Oil)</u>
<u>Refinery Processes</u>			
Combustion (heaters and boilers)	0.020	0.019	0.010
- Gas Fired	--	0.005	0.001
- Oil Fired	--	0.014	0.009
HDS	--	--	--
Tail Gas Treating	<u>0.003</u>	<u>--</u>	<u>--</u>
Subtotal	0.023	0.019	0.010
<u>Industrial Boiler Combustion</u>			
Residual Fuel Oil (No Control level)	<u>3.170</u>	<u>0.40</u>	<u>0.22</u>
Total	3.193	0.419	0.230

TABLE 6-4. ESTIMATED AIR EMISSIONS, 0.8% S FUEL OIL (MODERATE CONTROL LEVEL)
LB/10⁶ BTU FUEL OIL

<u>Emission Sources</u>	<u>SO_x</u> <u>(lb/10⁶ Btu Fuel Oil)</u>	<u>NO_x</u> <u>(lb/10⁶ Btu Fuel Oil)</u>	<u>Particulate</u> <u>(lb/10⁶ Btu Fuel Oil)</u>
<u>Refinery Processes</u>			
Combustion (heaters and boilers)	.020	.019	.010
- Gas Fired		.005	.001
- Oil Fired		.014	.009
HDS	.005	--	--
Tail Gas Treating/ Claus Plant	<u>.005</u>	<u>--</u>	<u>--</u>
Subtotal	0.030	0.019	0.010
<u>Industrial Boiler Combustion</u>			
Residual Fuel Oil (moderate control level)	<u>0.85</u>	<u>0.3</u>	<u>0.12</u>
Total	0.88	0.32	0.13

TABLE 6-5. ESTIMATED AIR EMISSIONS, 0.1% S FUEL OIL (STRINGENT CONTROL)
LB/10⁶ BTU FUEL OIL

<u>Emission Sources</u>	<u>(1b/10⁶ SO_x Btu Fuel Oil)</u>	<u>(1b/10⁶ NO_x Btu Fuel Oil)</u>	<u>(1b/10⁶ Particulate Btu Fuel Oil)</u>
<u>Refinery Processes</u>			
Combustion (heaters and boilers)	0.020	0.019	0.010
- Gas Fired		0.005	0.001
- Oil Fired		0.014	0.009
HDS	0.015	--	--
Tail Gas Treating/ Claus Plant	<u>0.015</u>	<u>--</u>	<u>--</u>
Subtotal	0.050	0.019	0.010
<u>Industrial Boiler Combustion</u>			
Residual Fuel Oil (stringent control level)	<u>0.11</u>	<u>0.11</u>	<u>0.05</u>
Total	0.16	0.13	0.06

TABLE 6-6. ESTIMATED AIR EMISSIONS - RESIDUAL FUEL OIL COMBUSTION

<u>Fuel Description</u>	<u>SO_x (LB/10⁶ BTU)</u>	<u>NO_x (LB/10⁶ BTU)</u>	<u>Particulate (LB/10⁶ BTU)</u>
3.0% Sulfur	3.18	0.40	0.22
1.0% Sulfur	1.06	0.33	0.14
0.8% Sulfur	.85	0.30	0.12
0.5% Sulfur	.53	0.25	0.09
0.2% Sulfur	.21	0.20	0.05
0.1% Sulfur	.11	0.18	0.03

6.3 WATER POLLUTION

The major use of water in petroleum refining is for steam generation and heat transfer. The volume of water coming in direct contact with process streams is small when compared with the water for indirect cooling and heat transfer. Nevertheless, nearly every major refining operation produces a wastewater stream containing various pollutants.

Major sources of contaminated water within the fuel oil refinery are sour water stripper condensate, contaminated process water, cooling tower blowdown, and desalter water. Each of these major sources is discussed below. Other potential contaminated water sources are oily process area storm water, oily cleaning water, and oily water from a ship's ballast, if the refinery is located near a docking facility. The combined wastewater from these sources is usually treated in a wastewater treating plant. Uncontaminated wastewater is also generated within the refinery. This water is handled separately from the contaminated water by a segregated wastewater system. The uncontaminated water, along with treated process wastewater, is retained in a holding pond for a certain period of time before discharge.

It is a typical practice in most refineries to collect all contaminated process wastewater and to combine it into a single wastewater stream and then to treat it in a central treatment facility. As a result of this, it is unnecessary to deal with the volume and characteristics of each of the component wastewater streams. Therefore, in assessing the water pollution implications of alterations to the base case refinery, it is not necessary to examine the individual wastewater sources. Rather, the volume and characteristics of the total refinery wastewater effluent will be examined. Table 6-7 gives the refinery effluent based upon 15 gallons of water required per barrel of crude feed.

Water Management

Water management at the refinery can exercise a number of strategies by direct implementation of several wastewater treatment processes. There are

TABLE 6-7. REFINERY WASTEWATER EFFLUENT QUALITY FOR
3 x 10⁶ GAL/DAY (200,000 BBL/DAY CRUDE FEED)

	<u>Concentration</u>
BOD	15 ppm
COD	80 ppm
Ammonia	2 ppm
Hydrogen Sulfide	0.1 ppm
Total Phosphorus	2 ppm
Phenols	0.1 ppm
Oil and Grease	2 ppm
Suspended Solids	10 ppm
Dissolved Solids	370 ppm

Source: "Environmental Problem Definition for Petroleum Refineries, Synthetic Natural Gas Plants, and Liquified Natural Gas Plants," Radian Corporation, November 1975, EPA-600/2-75-068.

four types of wastewater treatments applicable at the refinery: in-plant, primary, secondary, and tertiary. The degree to which each of these processes is utilized depends on the local area discharge regulations, the quality of wastewater effluents prior to treatment, and the degree of recycle or reuse of water desired. Table 6-8 shows a water management plan for a refinery and emphasizes some of the ways in which the wastewaters from various processes are segregated.

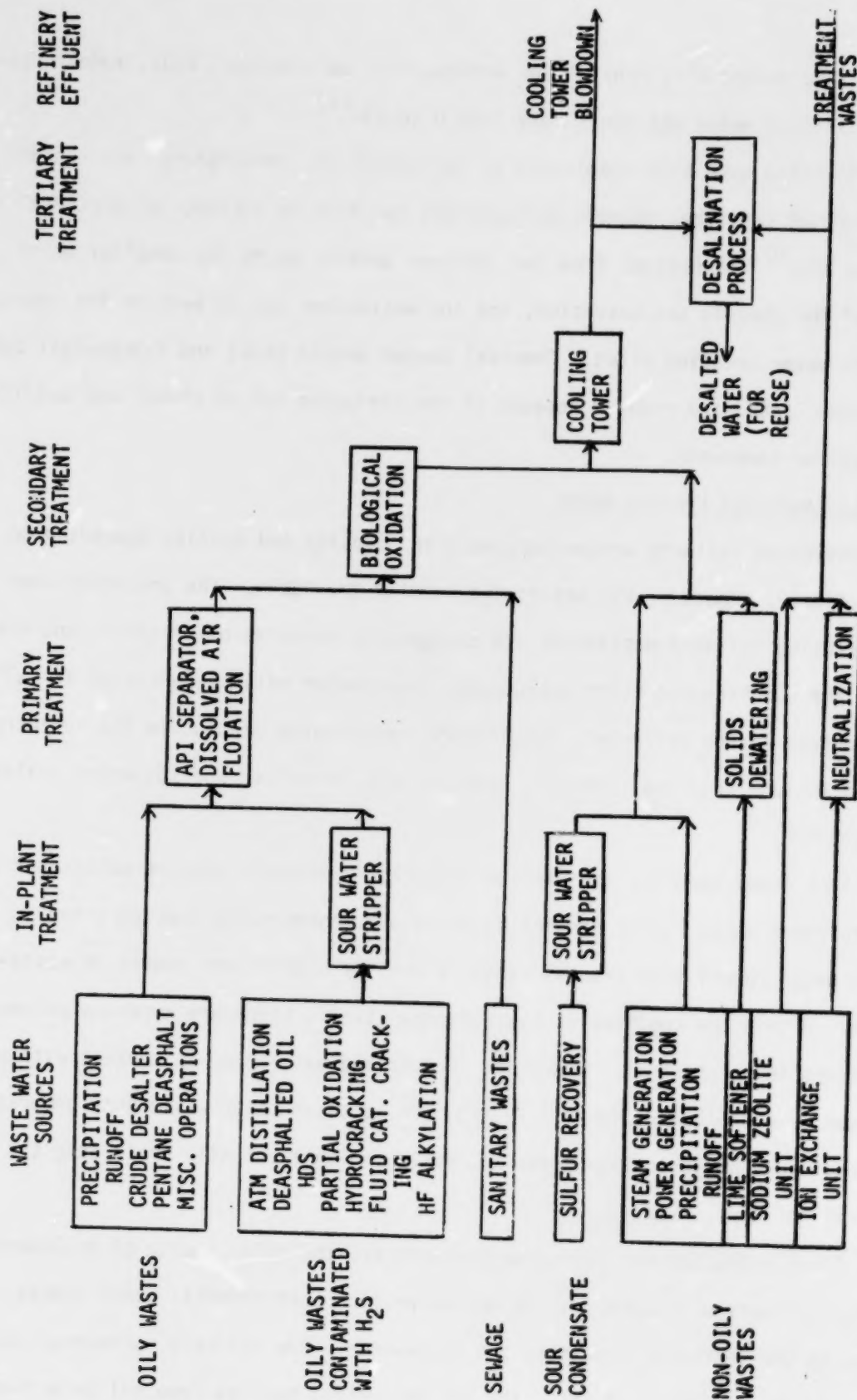
Sour Water Stripper Condensate

Sour or acid waters are produced in a refinery when steam is used as a stripping medium in the various cracking processes. The hydrogen sulfide, ammonia, and phenols distribute themselves between the water and hydrocarbon phases in the condensate. The concentrations of these pollutants in the water vary widely depending on crude sources and processing involved.⁽⁹⁾

The purpose of the treatment of sour water is to remove sulfides (as hydrogen sulfide, ammonium sulfide, and polysulfides) before the waste enters the sewer. The sour water can be treated by: stripping with steam or flue gas; air oxidation to convert hydrogen sulfide to thiosulfates; or vaporization and incineration. Due to the nature of the hydrodesulfurization process, the volume of direct contact process water discharged from the fuel oil refinery will not be significantly increased by producing lower sulfur fuels. The two main pollutants formed in hydrodesulfurization (hydrogen sulfide and ammonia) are both soluble in water and could be carried out with any wastewater streams. It is expected that these would be treated in the normal refinery ammonia and sour water strippers and that their contribution to the environmental impact can be estimated based on normal removal efficiencies of sulfide and ammonia using a well-controlled water management system.

Sour water strippers are designed primarily for the removal of sulfides and can be expected to achieve 85 to 99% removal. If acid is not required to enhance sulfide stripping, ammonia will also be stripped with the percentage varying widely with stripping temperature and pH. If acid is added to the

TABLE 6-8. REFINERY WATER MANAGEMENT PLAN



Source: Industrial Wastewater Management Handbook, H. S. Azad, IIS Corporation, McGraw-Hill Book Company, 1976, pp. 8-1 to 8-74.

wastewater, essentially none of the ammonia will be removed. Thus, ammonia removals in sour water strippers vary from 0 to 99%.⁽⁹⁾

Depending upon such conditions as wastewater pH, temperature, and contaminant partial pressure, phenols and cyanides can also be stripped with removal as high as 30%.⁽⁹⁾ The bottoms from the stripper usually go to the desalter where most of the phenols are extracted, and the wastewater can be sent to the regular process water treating plant. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are reduced because of the stripping out of phenol and oxidizable sulfur compounds.

Contaminated Process Water

Petroleum refinery wastewaters vary in quantity and quality depending on the refinery. However, the wastes are readily treatable. The processes used for treating refinery wastewater are designed to maximize oil recovery and minimize the discharge of other pollutants. Wastewater will be generated at multiple sources in the refinery. The primary contaminants present in the refinery's wastes include sulfides, ammonia, phenols, oil, dissolved and suspended solids, BOD and COD.

Tank farms used for the storage of refinery products produce wastewater streams due to storm water runoff contacting petroleum contaminated exposed areas. Storm water runoff from process areas is another significant source of wastewater. Within the confines of the refinery itself, there are numerous processing steps in which steam, condensate, or cooling water come in contact with petroleum or petroleum products. In addition to these major wastewater generation points, there are countless leaks and spills which eventually drain into the central refinery sewer system.

Since petroleum and petroleum products are the major source of pollutants in the refinery wastewater, it is not surprising that chemical constituents found in the petroleum appear in the wastewater. Raw refinery wastewater contains large quantities of oil. The oil is present both as free oil in a floatable form and as emulsified oil. In addition, water-soluble organics, such as

phenolic compounds which are present in the petroleum, will also be present in the wastewater from caustic scrubbing. Crude petroleum contains a variety of sulfur compounds which are removed from the finished product in varying degrees depending on product specifications.

For lower sulfur fuel oils, more of the sulfur compounds must be removed. Due to the oil/water contacting at various stages in the refinery operation, a significant quantity of sulfur compounds enters the wastewater stream.⁽¹⁰⁾ The most objectionable of these sulfur compounds are sulfides which are typically present in the wastewater as sulfide ions. Petroleum also contains a number of nitrogen-bearing compounds; and, therefore, refinery wastewater is typically contaminated with appreciable quantities of ammonia. Small amounts of cyanide compounds may also be expected to be present.⁽¹⁰⁾ Carbonaceous and inorganic particulate matter from a variety of sources are also present in refinery wastewater, thus contributing to the suspended solids level. Typical sources for the suspended solids emissions are incomplete combustion, soil, and the like. Most of the organic chemical compounds mentioned are oxidizable; and, therefore, refinery wastewater will exert a chemical oxygen demand. A certain fraction of the same compounds are biodegradable; and, therefore, refinery wastewater will also exert a biochemical oxygen demand. Petroleum also contains a variety of trace heavy metals; for example, mercury, cadmium, lead, and so forth, which vary greatly from crude to crude and have not been extensively quantified.

Hydrotreating processes in the refinery do not have any known effect on the quantity or quality of contaminated process water, except if flexicoking or delayed coking is used rather than direct hydrodesulfurization of the residua. The only adverse environmental effect is from the process water contacting the coke produced in flexicoking or delayed coking. The flexicoker produces a water purge from the Stretford process which incrementally increases the effluent wastewater load.⁽¹¹⁾

Cooling Tower Blowdown

All petroleum refineries use large amounts of non-contact cooling water. Due to the large volumes required, a cooling tower system is generally used to reuse most of the water. To prevent the buildup of naturally-occurring salts in the cooling water system, it is necessary to purge a portion of the total cooling water flow. Since it is a common practice to use corrosion inhibitors in the cooling circuit, cooling tower blowdown will contain such substances.

Depending on the type and quantity of corrosion inhibitor used in the non-contact cooling water circuit, the cooling water blowdown can present pollution problems of varying significance. The most common types of corrosion inhibitors contain chromate salts; thus, blowdown from cooling towers can often contain chromium in the form of hexavalent chromium, the more objectionable form.⁽¹⁰⁾ In the petroleum refining industry, there has been a continuing trend toward wastewater volume reduction to meet the zero discharge effluent guidelines. Large modern refineries generate far less wastewater than small old refineries because process improvements have decreased the volume of wastewater that must be treated. Improved leak and spill management, coupled with other preventive measures, has also contributed to the overall volume reduction. There has also been a trend toward tighter, non-contact cooling water circuits, in addition to more widespread use of air cooling.

The cooling water blowdown stream may be increased from 4 to 7% over that of the base case refinery due to the additional heat removal requirements associated with clean oil technologies such as direct hydrodesulfurization and flexicoking.⁽⁸⁾⁽¹¹⁾

Crude Desalter Water

Common to all types of desalting are an emulsifier and settling tank. Salts can be separated from oil by either of two methods. In the first method, water wash desalting in the presence of chemicals (specific to the type of

salts present and the nature of the crude oil) is followed by heating and gravity separation.

The continuous wastewater stream from a desalter contains emulsified, and occasionally free oil, ammonia, phenol, sulfides, and suspended solids. These pollutants produce a relatively high BOD₅ and COD. This wastewater also contains enough chlorides and other dissolved materials to contribute to the dissolved solids problem in the areas where the wastewater is discharged to fresh water bodies. There are also potential thermal pollution problems because the temperature of the desalting wastewater often exceeds 95°C (200°F).

However, hydrotreating processes make no further adverse environmental impact to the base refinery case.

6.4 SOLID WASTE

A petroleum refinery generates a wide variety of solid waste streams, many of which contain materials on the EPA toxic substances list. The nature and quantity of solid wastes emanating from refineries are highly variable and still the subject of much investigation. Basically, refinery solid waste streams fall into two main groups: those that are intermittently generated and those that are continuously generated.

Intermittent Wastes

Intermittent wastes are generally those that result from cleaning within the process areas and off-site facilities of the refinery. Typical intermittent waste streams may be processing vessel sludges, vessel scale, and other deposits generally removed during plant turnarounds, storage tank sediments, and product treatment wastes such as spent filter clay and spent catalysts from certain processing units such as hydrodesulfurization. The annual volume of refinery intermittent wastes is strongly a function of the individual refinery waste management and housekeeping practices.

Continuous Wastes

Continuous wastes, those that require disposal at least at two-week intervals, can be further broken down into two groups: process unit wastes and wastewater treatment wastes. Major process unit wastes include coker wastes, such as coke fines from fluidized cokers and spilled coke from unloading facilities, spent catalysts and catalyst fines from the fluid catalytic cracking units, and other spent or spilled wastes from processing plants. Water treatment wastes may include biological sludges from activated sludge units and dissolved air flotation "float" (DAF). Wastes from water treatment are generally dewatered by means of sludge thickeners, coupled with vacuum filters or centrifuges. The dewatered sludge can then either be land disposed or incinerated. Low concentrations of heavy metals are usually present in the sludges, which could affect the level of control required. There are many different types of refinery solid wastes, and there are many levels of technology for treatment and disposal of these petroleum refinery wastes.

The sludges present from washdown or processing operations require compliance with RCRA standards for toxic wastes, since they can contain trace amounts of nickel, vanadium, nickel carbonyl (or cobalt carbonyl depending on catalyst selection). Other compounds have been found in "floats" at levels which make its disposal complex: phenols, sulfides, phosphorus, ammonia, etc. Although incineration is the most desirable disposal alternative, the presence of heavy metals requires treatment prior to incineration and may make encapsulation/land disposal the viable disposal method. The existence of RCRA standards, the cost of land, and disposal operations costs place an additional penalty on the cost of desulfurization. Table 6-9 estimates emissions created during oily sludge incineration.

Wastes From Clean Oil Technology

There are only two individual refinery solid waste streams which have adverse environmental impacts at the refinery due to the production of low-sulfur

TABLE 6-9. SLUDGE INCINERATION EMISSIONS

<u>Pollutant</u>	<u>Emission (lb/1000 Gal Sludge)</u>
Particulate	23
SO ₂	47
CO	4
Hydrocarbons	3
NO _x	40

Source: "Environmental Problem Definition for Petroleum Refineries, Synthetic Natural Gas Plants, and Liquefied Natural Gas Plants," Radian Corporation, November 1975, EPA-600/2-75-068.

fuel oils. The worst of these individual solid waste streams is the increased amount of spent desulfurization catalysts which is sent to disposal. The second solid waste stream of concern is the increased waste from hydrogen manufacturing, due to the fact that additional hydrogen is needed to reduce the sulfur level in the product fuel oil.

A number of refinery processes require the use of a fixed-bed catalyst. These processes include catalytic reforming, hydrodesulfurization, hydrotreating, hydrocracking, steam hydrocarbon reforming for hydrogen production, sulfur production from H_2S and/or SO_2 , and others. These catalysts eventually become inactive and are replaced in the reactors with fresh catalysts during a unit shutdown. Catalyst life may extend from six months to as long as three years. Many of these catalysts contain valuable metals which can be recovered economically. Some of these metals, such as platinum and palladium, represent the active catalytic component. Others are contaminants in the feed, which are adsorbed on the catalyst during use. Usually, the more valuable metals are recovered by an outside company before the spent catalysts are disposed of as solid wastes by these companies. In addition to hydrodesulfurization and demetallization catalysts, additional sulfur removal from the product fuel oil will produce an increase in the amount of spent Claus catalyst to be disposed.

The disposal of hydrodesulfurization spent catalysts is clearly the largest solid waste problem associated with hydrotreating; however, an estimate of finite amounts of contamination from catalyst disposal is not available from the literature surveyed. This impact study is limited to the point at which the spent catalyst quantity emanating from the refinery has been identified as a solid waste. The impact of spent catalyst use is the subject of an existing EPA contract on Environmental Assessment for Residual Oil Utilization.⁽¹²⁾

Without going into specific disposal techniques, several general statements can be made about the HDS catalyst use for the U. S. Based upon 600,000 BPSD Residual and VGO hydrodesulfurization capacity, an estimation of total nationwide spent catalyst can be made. The following table estimates the total possible spent catalyst generation for the 600,000 BPSD HDS processes:

	Spent Catalyst Generation for Sulfur Control Levels in Tons/Yr		
	<u>0.8% S LSFO</u>	<u>0.3% S LSFO</u>	<u>0.1% S LSFO</u>
1. Low Sulfur, High Metals	20,000	64,000	115,000
2. High Sulfur, High Metals	38,000	69,000	125,000
3. Low Sulfur, Low Metals	8,000	11,000	13,000
4. High Sulfur, Low Metals	17,000	29,000	38,000

Since most off-site or in-situ regeneration techniques recover 90-96% of the catalyst activity, the estimated make-up amounts equal the catalyst requiring ultimate disposal. Thus, for a worst-case scenario, 10% catalyst loss per year would be a 12,500 tons per year disposal amount. This closely correlates with an estimated market of 10,000-12,000 tons/yr for HDS catalysts made by catalyst manufacturers and regeneration firms.⁽¹³⁾

The rapid growth of HDS processes has increased the demand for hydrogen beyond the level of byproduct H_2 available from steam reforming and other processes. Refinery off-gases are utilized as a charge stock for H_2 production by passing the gas over a three-bed desulfurization unit containing a first-stage zinc oxide, second-stage cobalt/moly catalyst, followed by a third-stage zinc oxide bed. The spent zinc oxide and cobalt/moly catalysts then become a solid waste due to HDS requiring additional hydrogen.

Catalyst disposal presents much the same problem as the sludge or "float" wastes previously mentioned except that its relative toxicity is far greater, since much of the material is heavy metals. The effect of the metallic nature for disposal means that very stringent RCRA standards will be applied to any disposal operation. The rising costs for nickel, cobalt, and molybdenum make in-situ or off-site regeneration more cost-effective alternatives. The operational cost for an RCRA quality disposal site for these contaminated catalysts could be in the \$30-50/ton range.

The most common regeneration method is steam-air application at temperatures approaching 900°F in order to burn off the carbon/coke build-up. Generally, a single burn with a steam-air mixture will reduce the residual carbon from 12-15% by weight to 1.5-3.0% by weight. If lower residual carbon levels are required by the HDS operation, at least two or three modest increases in inlet temperature and oxygen levels should be made to see if any secondary combustion can be achieved. Steam rates should be maximized for the best possible flow distribution, and an indicator of steam flow is usually about 1 lb steam/hour/ lb catalyst. Inlet oxygen concentrations should not exceed 2%, since hitting a pocket of previously-untouched catalyst could trigger runaway burning. After regeneration, the cooling medium should not be switched to air until the catalyst is cooled to about 400°F. (14)

Both off-site and in-situ regeneration are receiving rapidly-growing acceptance for several reasons:

- (1) Quality - The catalyst suffers severe activity loss due to the action of the steam. In the case of nitrogen-air in-situ regeneration, unscreened catalyst will have poor flow distribution; and, the resulting localized high temperatures destroy catalyst activity.

- (2) Cost - Off-site and in-situ regeneration require minimal catalyst replacement; thus, the savings due to regeneration from a large refinery complex can be considerable if the alternative is to throw away the catalyst. In-situ regeneration causes extensive unit downtime unless multiple parallel units exist, which increases initial capital outlay. If approximately 15 days are needed for in-situ regeneration, the lost downtime could easily approach \$1,500,000. Although off-site regeneration minimizes plant downtime, additional replacement catalyst is required. At a rate of \$1.80/lb for catalyst and using a 75,000 barrel/day atmospheric residual HDS unit requiring 4,000,000 lbs catalyst, the inventory cost of catalyst needed for off-site regeneration is \$7,200,000. As previously stated, multiple units would allow for regeneration while minimizing the need for spare catalyst; but, capital expenditures for the HDS facility would increase due to multiple equipment requirements.

Using 25,000 barrels/day/desulfurization train as a guideline, the three trains required for the 75,000 BPSD refinery would allow for off-site or in-situ regeneration to be performed with minimal downtime. By rotating regeneration sequence, the actual monetary loss from such downtime is considerably smaller than complete shutdown or catalyst replacement expenses.

Off-site regeneration charges of 45-55¢/lb are approximately 25-30% of new catalyst cost. Thus, the savings for the refiner are in the \$1.25-\$1.35/lb

neighborhood, (15) which makes regeneration worth examination when compared to complete catalyst disposal.

- (3) Pollution - Off-site regeneration facilities are equipped to control air and water pollution problems. Opting for off-site regeneration removes a pollution problem from the refiner, since unusable catalyst disposal is no longer his responsibility. In addition, the construction of extra pollution abatement facilities in the refinery, where they will be used only during infrequent catalyst regeneration, is not economically sound.

Although this discussion centers on regeneration for removal of carbon/coke build-up, the deposition of metals in the catalyst pores from HDS processing of a high metals content residual enhances the need for restoring catalyst activity periodically and for recovery of saleable metals. With the HDS processing activity increase in recent years, a substantial market has developed for metals recovery. Several firms now provide off-site metals reclamation services. Higher prices for cobalt and nickel-tungsten catalysts provide a credit for the HDS processor in that the amount of metal recovered offsets the cost of replacement catalyst. However, the off-site recovery operation means that refiners will have to carry extra catalyst inventory, which, in the case of large HDS units, could amount to substantial capital outlay, as previously discussed in the case of off-site regeneration. The same off-site regeneration cost figures apply for metals recovery, but metals-value credits will help reduce the regeneration cost.

Factors Affecting Solid Waste

There are several important factors affecting solid waste generation at the refinery. The type of crude stock is one of the most important. The constituents of crude oil can vary widely. The heavy metal content, for example,

is of major importance in determining the hazardous or potentially-hazardous metal content in crude oil storage tank bottoms, in spent catalysts, and in the various wastewater treatment plant sludges. It is therefore reasonable to expect that solid wastes will contain different concentrations of potentially-hazardous materials and that such differences may even be reflected in the solid waste loads of two refineries of equal capacity which produce the same products but utilize different crude mixes.

A second factor affecting solid waste generation is the variation of process types; for example, differences in wastewater and air pollution control processes will affect the quantity as well as the composition of potentially-hazardous waste material. There are differences, also, in the degree and type of wastewater treatment processes employed by refineries. A refinery using an extended aeration sludge activation system will generate smaller quantities of biological sludges than will a refinery which utilizes a conventional activated sludge system. Refineries using only primary wastewater treatment before discharging into a municipal treating system do not generate the biological sludges which are associated with secondary treatment.

A third factor affecting solid waste generation is the age of the processes in the refinery. Process age refers to the general technology used in the process rather than to the length of time the process has been in service. This technology includes methods that will increase or decrease the quantity of solid waste. For example, the use of air instead of water cooling will reduce or eliminate a solid waste problem from the cooling tower sludges.⁽¹⁶⁾

6.5 OTHER ENVIRONMENTAL IMPACTS

Most refineries generate fairly high noise levels within the battery limits because of equipment such as pumps, compressors, steam jets, flare stacks, and so forth. Any equipment or equipment changes associated with the production of low-sulfur fuel oil or associated with in-process control systems would not

significantly add to these noise levels. There are many practical industrial approaches to controlling refinery noise. However, the cost of noise abatement in the overall refinery pollution abatement program would be a substantial item. (17)(18)

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EMISSION SOURCE TEST DATA

7.1 INTRODUCTION

This section contains a summary of the available emission source test data gathered during the development of the proposed industrial boiler standards. Included are descriptions of the facilities tested, identification of the test methods, and the data obtained.

The majority of the data available for oil-fired industrial boiler emissions was found in References 1-3, which document a study of pollution control by combustion modification, with emphasis on NO_x control. The test methods used were selected according to the pollutant being measured. Particulate emissions were measured by EPA Reference Method 5, SO_x by wet chemical analysis using the "Shell-Emeryville" method, and NO_x by a chemiluminescent nitric oxide analyzer. Opacity was measured in some cases, using Bacharach Smoke Spots. The test facilities were oil-fired industrial boilers with capacities less than 250 MBtu/hr.

Some particulate emission data were also available from Reference 5, a study of particulate emission control systems for oil-fired boilers.

7.2 TEST RESULTS

The available source test data for SO_x , NO_x , and particulate emissions from oil-fired industrial boilers are presented in Tables 7-1, 7-2, and 7-3, respectively. Most of the control methods indicated refer to combustion modification for NO_x control. Baseline refers to boiler runs at approximately 80% of rated capacity, with no emission control techniques employed. Only one set of data is available for each set of conditions at each location, so the single values are listed under the "average" column. Data on the duration of the test runs were not available. Percent control and design control efficiency are not meaningful, since the boilers are uncontrolled. A value for percent control could be calculated, however, based on the emission of all of the fuel

TABLE 7-1. EMISSION SOURCE TEST DATA - SO_x

Actual Pilot Size 10 ³ lb/hr.	Test Load 10 ³ lb/hr.	Control Method	Fuel Characteristics			No. or Dur- ation of Tests	Longest Cont. Duration	Emissions (lb/H8tu) (ng/J)			% Control Based on Average of All Tests	Design Control Effi- ciency of Device	Control Levels Sup- ported*	Reference Unit I.D. & Location	Test No.	Ref.
			Heat Value Btu/lb	% S	% Ash			Low	High	Average						
110	80	Baseline	19,340	.18	.004	1	No Data			.195	No Data	No Data	S	Unit 1-8; Loc. 17	7-10	1
80	51	Baseline	18,500	1.49	.019	1	"			.858	"	"	SIP	Unit 4; Loc. 20	8-5	1
90	71	Baseline	18,420	1.04	.031	1	"			.063	"	"	SIP	Unit 2; Loc. 18	9-1	1
65	54	Baseline & H ₂ Load	18,930	--	.043	1	"			.869	"	"	SIP	Unit 2; Loc. 16	10-2	1
105	80	Baseline	18,910	1.03	.032	1	"			.902	"	"	SIP	Unit 3; Loc. 18	21-6	1
160	130	Baseline	18,910	1.03	.032	1	"			.969	"	"	SIP	Unit 4; Loc. 18	22-1	1
500	400	Baseline	18,330	2.43	.12	1	"			2.68	"	"	--	Unit 2; Loc. 13	29-5	1
10	7	Baseline & H ₂ Load	--	.23	--	1	"			.159	"	"	S	Unit 2; Loc. 3	33-3	1
7	6.7	Baseline & H ₂ Load	18,280	1.85	.038	1	"			2.01	"	"	--	Unit 1; Loc. 23	34-11	1
17.5	14	Baseline	19,470	.06	.001	1	"			.111	"	"	S	Unit 1; Loc. 19	52-5	1
20	14	H ₂ Air	19,470	.06	.001	1	"			.123	"	"	S	Unit 1; Loc. 19	53-6	1
158	16	Baseline	--	.30	--	1	"			.198	"	"	I	Unit 4; Loc. 4	59-6	1
33	115	Baseline	--	--	.005	1	"			.168	"	"	S	Unit 3; Loc. 6	65-1	1
17.5	23	Baseline	19,440	.40	.003	1	"			.198	"	"	S	Unit 3; Loc. 1	66-1	1
17.5	14.5	Baseline	19,680	.16	.001	1	"			.180	"	"	S	Loc. 19	19-5	3
17.5	14.5	Low O ₂	19,610	.14	.001	1	"			.238	"	"	I	Loc. 19	19-74	3
17.5	14.5	FGR; Low O ₂	19,610	.14	.001	1	"			.177	"	"	S	Loc. 19	19-83	3
17.5	14.5	Staged Air	19,610	.14	.001	1	"			.159	"	"	S	Loc. 19	19-116	3
17.5	14.3	FGR & SA	19,610	.14	.001	1	"			.200	"	"	S	Loc. 19	19-179	3
17.5	13.8	Low O ₂	19,000	.54	.019	1	"			.580	"	"	M	Loc. 19	19-97	3
17.5	14.2	Baseline	18,780	.60	.034	1	"			.744	"	"	M	Loc. 19	19-132	3
17.5	13.8	Low O ₂	18,780	.60	.034	1	"			.660	"	"	M	Loc. 19	19-143	3
17.5	14.0	Max. FGR	18,780	.60	.034	1	"			.627	"	"	M	Loc. 19	19-159	3
17.5	14.3	FGR & SA	18,780	.60	.034	1	"			.665	"	"	M	Loc. 19	19-170	3
45	38.0	Baseline	18,467	1.88	.05	1	"			1.77	"	"	--	Loc. 33	200-24	3
45	38.8	Low O ₂	18,467	1.88	.05	1	"			1.75	"	"	--	Loc. 38	201-12	3
45	38	Staged Comb. Air	18,467	1.88	.05	1	"			1.86	"	"	--	Loc. 38	203-26A	3
45	38.8	Low O ₂	18,467	1.88	.05	1	"			1.89	"	"	--	Loc. 38	201-15	3
29	17	Baseline	19,440	.40	.003	1	"			.438	"	"	I	Loc. 1	102-6	2
29	25	Baseline	19,440	.40	.003	1	"			.699	"	"	M	Loc. 1	107-2	2

TABLE 7-7. EMISSION SOURCE TEST DATA - SO_x (cont'd.)

Actual Boiler Size 10 ³ lb/hr	Test Load 10 ³ lb/hr	Control Method	Fuel Characteristics			No. or Dur- ation of Tests	Longest Cont. Duration	Emissions (lb/Mbtu)			% Control Based on Average of All Tests	Design Control Effi- ciency of Device	Control Levels Sup- ported*	Reference Unit I.D. & Location	Tsst No.	Ref.
			Heat Value Btu/lb	% S	% Ash			Low	High	Average						
150	70	800S	18,213	2.74	.03	1	No Data			2.37	No Data	No Data	--	Loc. 29	119-6	2
70	30	Variable Preheat	--	--	--	1	"			2.42	"	"	--	Loc. 28	130-1	2
40	32	Baseline	18,773	1.91	.07	1	"			1.90	"	"	--	Loc. 37	176-2	2
45	36	Baseline	19,227	.19	.08	1	"			1.72	"	"	--	Loc. 38	186-1	2
17.5	14	Baseline	19,565	.37	.009	1	"			.340	"	"	I	Loc. 19	200-3	2

* S = Stringent = .2 lb/Mbtu
I = Intermediate = .5 lb/Mbtu
M = Moderate = .8 lb/Mbtu

Thus, S, I, and M all meet SIP levels.

Source: Personal communication from Acurex, 8-29-78.

TABLE 7-2. EMISSION SOURCE TEST DATA - NO_x

Fuel Characteristics															No. or Dur- ation of Tests	Longest Cont. Duration	Emissions (lb/MBtu) (ng/J)			% Control Based on Average of All Tests	Design Control Effi- ciency of Device	Control Levels Sup- ported*	Reference Unit I.D. & Location	Test No.	Ref.
Actual Boiler Size 10 ³ lb/hr	Test Load 10 ³ lb/hr	Control Method	Heat Value Btu/lb	% Ash		Test Method	Low			High			Average												
				%S	% Ash		Low	High	Average																
110	88	Baseline	19,340	.18	.004	Chemiluminescence	1	No Data			.227	No Data	No Data	SIP	Unit T-8	7-10	1								
80	51	Baseline	18,560	1.53	.032	Chemiluminescence	1	No Data			.391	No Data	No Data	--	Loc. 17	8-5	1								
90	71	Baseline	18,420	1.04	.031	Chemiluminescence	1	No Data			.316	No Data	No Data	--	Unit 4	9-1	1								
65	54	Baseline Hi Load	18,930	1.03	.043	Chemiluminescence	1	No Data			.239	No Data	No Data	M	Loc. 18	10-2	1								
105	80	Baseline	18,910	1.03	.032	Chemiluminescence	1	No Data			.322	No Data	No Data	--	Loc. 16	21-6	1								
105	76	#4 B00S	18,910	1.03	.032	Chemiluminescence	1	No Data			.285	No Data	No Data	M	Loc. 18	21-20	1								
160	130	Baseline	18,910	1.03	.032	Chemiluminescence	1	No Data			.308	No Data	No Data	--	Unit 3	27-1	1								
160	105	#2 B00S	18,910	1.03	.032	Chemiluminescence	1	No Data			.250	No Data	No Data	M	Unit 4	22-16	1								
500	400	Baseline	18,330	2.43	.12	Chemiluminescence	1	No Data			.342	No Data	No Data	--	Loc. 18	29-5	1								
10	7	Baseline	--	.23	--	Chemiluminescence	1	No Data			.217	No Data	No Data	SIP	Unit 2	33-3	1								
7	6.7	Baseline Hi Load	18,280	1.85	.038	Chemiluminescence	1	No Data			.383	No Data	No Data	--	Loc. 3	34-11	1								
17.5	14	Baseline	19,470	.06	.001	Chemiluminescence	1	No Data			.084	No Data	No Data	S	Unit 1	52-5	1								
17.5	14	Hi Air	19,470	.06	.001	Chemiluminescence	1	No Data			.131	No Data	No Data	I	Loc. 19	53-6	1								
17.5	12	Baseline	19,470	.06	.001	Chemiluminescence	1	No Data			.102	No Data	No Data	I	Unit 1	54-5	1								
20	16	Baseline	--	.30	--	Chemiluminescence	1	No Data			.248	No Data	No Data	SIP	Unit 4	59-6	1								
158	115	Baseline	--	.23	.005	Chemiluminescence	1	No Data			.232	No Data	No Data	SIP	Unit 3	65-1	1								
33	23	Baseline	--	.22	.001	Chemiluminescence	1	No Data			.158	No Data	No Data	M	Unit 3	66-1	1								
17.5	14.5	Baseline	19,680	.16	<.001	Chemiluminescence	1	No Data			.157	No Data	No Data	M	Loc. 1	19-5	3								
17.5	14.5	Low O ₂	19,610	.14	.001	Chemiluminescence	1	No Data			.127	No Data	No Data	I	Loc. 19	19-74	3								

TABLE 7-2. EMISSION SOURCE TEST DATA - NO_x (cont'd.)

Actual Boiler Size 103 lb/hr	Test Load 103 lb/hr	Fuel Characteristics			No. or Dur- ation of Tests	Longest Cont. Duration	Emissions (lb/Mbtu)			% Control Based on Average of All Tests	Design Control Effi- ciency of Device	Control Levels Sup- ported*	Reference Unit I.D. & Location	Test No.	Ref.
		Heat Value Btu/lb	% Ash	% S			Low	High	Average						
17.5	14.5	FGR	19,610	.14	.001	Chemiluminescence	1	No Data	.041	No Data	No Data	S	Loc. 19	19-83	3
	14.5	Low O ₂ Staged Air	19,610	.14	.001	Chemiluminescence	1	No Data	.126	No Data	No Data	I	Loc. 19	19-116	3
	14.3	FGR & SA	19,610	.14	.001	Chemiluminescence	1	No Data	.042	No Data	No Data	S	Loc. 19	19-179	3
17.5	13.8	Low O ₂ Baseline	19,000	.54	.019	Chemiluminescence	1	No Data	.280	No Data	No Data	M	Loc. 19	19-97	3
17.5	14.2	Low O ₂ Staged	18,780	.60	.034	Chemiluminescence	1	No Data	.196	No Data	No Data	I	Loc. 19	19-132	3
17.5	13.8	Low O ₂ Staged	18,780	.60	.034	Chemiluminescence	1	No Data	.198	No Data	No Data	I	Loc. 19	19-143	3
17.5	14.0	Max. FGR	18,780	.60	.034	Chemiluminescence	1	No Data	.196	No Data	No Data	I	Loc. 19	19-159	3
17.5	14.3	FGR & SA	18,780	.60	.034	Chemiluminescence	1	No Data	.211	No Data	No Data	M	Loc. 19	19-170	3
29	17	Baseline	19,440	.40	.003	Chemiluminescence	1	No Data	.118	No Data	No Data	I	Loc. 1	102-6	2
29	25	Baseline	19,440	.40	.003	Chemiluminescence	1	No Data	.111	No Data	No Data	I	Loc. 1	107-2	2
150	70	Low Load	18,213	2.74	.03	Chemiluminescence	1	No Data	.324	No Data	No Data	--	Loc. 29	119-1	2
150	70	BOOS	18,213	2.74	.03	Chemiluminescence	1	No Data	.242	No Data	No Data	M	Loc. 29	119-6	2
70	29	Baseline	--	--	--	Chemiluminescence	1	No Data	.268	No Data	No Data	M	Loc. 28	126-2	2
70	30	Variable	--	--	--	Chemiluminescence	1	No Data	.322	No Data	No Data	--	Loc. 28	130-1	2
200	68	Temp.	19,390	.31	<.001	Chemiluminescence	1	No Data	.135	No Data	No Data	I	Loc. 36	160-1	2
	62	Baseline	18,660	1.6	.25	Chemiluminescence	1	No Data	.345	No Data	No Data	--	Loc. 20	170-3	2
	40	Baseline	18,773	1.91	.07	Chemiluminescence	1	No Data	.254	No Data	No Data	M	Loc. 37	176-2	2
40	32	Low Air	18,773	1.91	.07	Chemiluminescence	1	No Data	.227	No Data	No Data	M	Loc. 37	179-4	2
45	36	Baseline	19,227	.19	.08	Chemiluminescence	1	No Data	.426	No Data	No Data	--	Loc. 38	186-1	2
45	36	SCA	19,227	.19	.08	Chemiluminescence	1	No Data	.226	No Data	No Data	M	Loc. 38	188-1	2
45	36	SCA	19,365	.37	.009	Chemiluminescence	1	No Data	.221	No Data	No Data	M	Loc. 38	195-1	2
17.5	14	Baseline	19,365	.37	.009	Chemiluminescence	1	No Data	.175	No Data	No Data	I	Loc. 19	198-12	2
17.5	14.3	SCA	19,365	.37	.009	Chemiluminescence	1	No Data	.212	No Data	No Data	M	Loc. 19	200-3	2
17.5	14.0	Baseline	19,365	.37	.009	Chemiluminescence	1	No Data	.170	No Data	No Data	I	Loc. 19	203-7	2
17.5	14.0	SCA	19,365	.37	.009	Chemiluminescence	1	No Data	.170	No Data	No Data	I	Loc. 19	203-7	2

* S = Stringent = .1 lb/Mbtu for F.O. #6 and F.O. #2

I = Intermediate = .2 lb/Mbtu for F.O. #6;

.15 lb/Mbtu for F.O. #2

M = Moderate = .3 lb/Mbtu for F.O. #6

.2 lb/Mbtu for F.O. #2

SIP = 0.3 lb/Mbtu

Thus, S, I, and M all meet SIP levels.

Source: Personal communication from Acurex, 8-29-78.

TABLE 7-3. EMISSION SOURCE TEST DATA - SOLID PARTICULATE

Actual Boiler Size 10 ³ lb/hr	Test Load 10 ³ lb/hr	Fuel Characteristics			Test Method	No. or Duration of Tests	Longest Cont. Duration	Emissions (lb/HgCu) (ng/J)			% Control Based on Average of All Tests	Design Control Efficiency of Device	Control Levels Sup- ported*	% Opacity Smoke Spot Number	Reference Unit I.D. & Location	Test No.	Ref.
		Heat Value Btu/lb	% S	% /sn				Low	High	Average							
110	88	19,340	1.18	.004	EPA 5	1	No Data			.0103	"	"	S	--	Unit 4; Loc. 20	7-10	1
80	51	18,500	1.49	.019	"	1	"			.0704	"	"	I	--	Unit 4; Loc. 18	8-5	1
90	71	18,420	1.04	.031	"	1	"			.0912	"	"	M	--	Unit 2; Loc. 16	9-1	1
65	54	18,930	--	.043	"	1	"			.1045	"	"		--	Unit 2; Loc. 16	10-2	1
105	80	18,910	1.03	.032	"	1	"			.0581	"	"	I	--	Unit 3; Loc. 18	21-6	1
105	76	18,910	1.03	.032	"	1	"			.0901	"	"	I	--	Unit 3; Loc. 18	21-20	1
160	130	18,910	1.03	.032	"	1	"			.0385	"	"	I	--	Unit 4; Loc. 18	22-1	1
160	105	18,910	1.03	.032	"	1	"			.0485	"	"	I	--	Unit 4; Loc. 18	22-16	1
500	400	18,530	2.43	.12	"	1	"			.3596	"	"	--	--	Unit 2; Loc. 13	29-5	1
10	7	--	.23	--	"	1	"			.0205	"	"	S	--	Unit 2; Loc. 3	33-3	1
7	6.7	18,280	1.85	.038	"	1	"			.207	"	"	M	2.3	Unit 1; Loc. 23	34-11	1
17.5	14	19,470	.06	.001	"	1	"			.0339	"	"	I	--	Unit 1; Loc. 19	52-5	1
17.5	14	19,470	.06	.001	"	1	"			.0163	"	"	S	--	Unit 1; Loc. 19	53-6	1
17.5	12	19,470	.06	.001	"	1	"			.0151	"	"	S	--	Unit 1; Loc. 19	54-5	1
20	16	--	.30	--	"	1	"			.0145	"	"	S	--	Unit 4; Loc. 4	59-6	1
158	115	--	--	.005	"	1	"			.0037	"	"	S	--	Unit 3; Loc. 6	65-1	1
33	23	19,440	.40	.003	"	1	"			.0246	"	"	S	--	Unit 3; Loc. 1	66-1	1
17.5	14.5	19,680	.16	.001	"	1	"			.006	"	"	S	0%	Loc. 19	19-5	3
17.5	14.5	19,610	.14	.001	"	1	"			.0138	"	"	S	0%	Loc. 19	19-74	3
17.5	14.5	19,610	.14	.001	"	1	"			.0045	"	"	S	0%	Loc. 19	19-83	3
17.5	14.5	19,610	.14	.001	"	1	"			.0210	"	"	S	13%	Loc. 19	19-116	3
17.5	14.3	19,610	.14	.001	"	1	"			.0077	"	"	S	0%	Loc. 19	19-179	3
17.5	13.8	19,000	.54	.019	"	1	"			.064	"	"	I	0%	Loc. 19	19-97	3
17.5	14.2	18,780	.60	.034	"	1	"			.060	"	"	I	6%	Loc. 19	19-132	3
17.5	13.0	18,780	.60	.034	"	1	"			.064	"	"	I	22%	Loc. 19	19-143	3
17.5	14.0	18,780	.60	.034	"	1	"			.065	"	"	I	0%	Loc. 19	19-159	3
17.5	14.3	18,780	.60	.034	"	1	"			.021	"	"	S	0%	Loc. 19	19-170	3
45	38.0	18,467	1.83	.05	"	1	"			.083	"	"	I	--	Loc. 38	200-24	3
45	38.8	18,467	1.88	.05	"	1	"			.083	"	"	I	--	Loc. 38	201-12	3
45	34	18,467	1.88	.05	"	1	"			.037	"	"	I	--	Loc. 38	202-4	3

TABLE 7-3. EMISSION SOURCE TEST DATA - SOLID PARTICULATE (cont'd.)

Actual Boiler Size 10 ³ lb/hr	Test Load 10 ³ lb/hr	Control Method	Fuel Characteristics			No. or Dur- ation of Tests	Longest Duration Cont.	Emissions (lb/MBtu) (mg/J)			% Control Based on Average of All Tests	Design Control Effi- ciency of Device	Control Levels Sub- ported*	% Opacity Smoke Spot Number	Reference Unit I.D. & Location	Test No.	Ref.
			Heat Value Btu/lb	\$ S	Ash %			Low	High	Average							
45	38	Staged Comb. Air	18,467	1.88	.05	1	No Data			.09	No Data	No Data	I	--	Loc. 38	203-26A	3
45	39	Staged Comb. Air	18,467	1.88	.05	1	"			.092	"	"	I	--	Loc. 38	203-268	3
45	38.8	Low O ₂	18,467	1.88	.05	1	"			.089	"	"	I	--	Loc. 38	201-15	3
29	17	Baseline	19,440	.40	.003	1	"			.017	"	"	S	--	Loc. 1	102-6	2
29	25	Baseline	19,440	.40	.003	1	"			.011	"	"	S	--	Loc. 1	107-2	2
150	70	Low Load	18,213	2.74	.03	1	"			.044	"	"	I	--	Loc. 29	119-1	2
70	29	Baseline	--	--	--	1	"			.296	"	"	--	5.5	Loc. 28	126-2	2
70	30	Variable	--	--	--	1	"			.108	"	"	M	3.0	Loc. 28	130-1	2
200	60	Preheat	19,390	.31	.001	1	"			.016	"	"	S	0.0	Loc. 36	160-1	2
80	62	Baseline	18,660	1.6	.25	1	"			.074	"	"	I	3.0	Loc. 20	170-3	2
40	32	Baseline	18,773	1.91	.07	1	"			.118	"	"	M	5.0	Loc. 37	176-2	2
40	40	Low Air	18,773	1.91	.07	1	"			.081	"	"	I	7.0	Loc. 37	179-4	2
45	36	Baseline	19,227	.19	.08	1	"			.090	"	"	I	--	Loc. 38	186-1	2
45	36	SCA	19,227	.19	.08	1	"			.128	"	"	M	8.0	Loc. 38	188-1	2
17.5	14	Baseline	19,365	.37	.009	1	"			.020	"	"	S	1.5	Loc. 19	195-1	2
17.5	14.4	FGR	19,365	.37	.009	1	"			.022	"	"	S	--	Loc. 19	197-8	2
17.5	14.3	SCA	19,365	.37	.009	1	"			.023	"	"	S	4.0	Loc. 19	198-12	2
17.5	14.0	Baseline	19,365	.37	.009	1	"			.032	"	"	I	1.0	Loc. 19	200-3	2
17.5	14.0	SCA	19,365	.37	.009	1	"			.042	"	"	I	8.0	Loc. 19	203-7	2
169	No Data	Electrostatic Precipitator	--	.86	--	1	"			.074	"	"	I	--	Co. A, Plant 1	--	5
169	"	"	--	1.18	--	1	"			.142	"	"	M	--	Co. A, Plant 1	--	5
169	"	"	--	1.13	--	1	"			.150	"	"	M	--	Co. A, Plant 1	--	5
188	"	"	--	1.00	--	1	"			.097	"	"	I	--	Co. A, Plant 1	--	5
94	"	"	--	.70	--	1	"			.055	"	"	I	--	Polaroid, New Bedford	--	5
94	"	"	--	.70	--	1	"			.070	"	"	I	--	Polaroid, New Bedford	--	5

* S = Stringent = .03 lb/Mbtu
I = Intermediate = .10 lb/Mbtu
M = Moderate = .25 lb/Mbtu

Thus, S and I meet SIP level.

Source: Personal communication from Acurex, 8-29-78.

nitrogen or sulfur as NO_x or SO_x ; but, the value of this number is questionable. A blank in the "Control Levels Supported" column indicates that no control levels are supported.

7.3 TEST METHODS

Particulate samples were taken with a Joy Manufacturing Co. Portable Effluent Sampler, which meets design specifications for EPA Test Method 5 (Federal Register, Volume 36, No. 27, p. 24888, December 23, 1971). Dry particulates were collected in a heated case containing a cyclone for separation of particles larger than 5 microns, followed by a 125 mm glass fiber filter for retention of particles down to 0.3 microns. A train of 4 Greenburg-Smith impingers in a chilled water bath was used to collect condensible particulates. Since EPA standards are based on solid (dry) particulate, only the dry particulate values are considered in this report.

The measured values of particulate in lb/ft^3 were converted to lb/MBtu , using the revised method promulgated by EPA (Federal Register, Volume 39, No. 177, Part II, paragraph 60.46, September 11, 1974), which utilizes a fuel analysis and the measured excess O_2 in the exhaust, to calculate the gas volume generated in liberating a million Btu's. This method also includes excess air dilution.

SO_3 concentrations were measured by wet chemical analysis using the "Shell-Emeryville" method. The gas sample is drawn through a heated glass probe containing a quartz wool filter to remove particulate matter, into three sintered glass plate absorbers. The sulfur trioxide is removed by the first two absorbers containing aqueous isopropyl alcohol, and the sulfur dioxide is removed by the last absorber containing aqueous hydrogen peroxide. Separation of the components is completed by a nitrogen purge of the absorbers, to transfer all remaining SO_2 to the third absorber. The sulfate from the SO_3 and SO_2 absorbers is then titrated with standard lead perchlorate solution, using Sulfonazo III indicator.

Total nitrogen oxides were measured by a Thermo-Electron brand chemiluminescent nitric oxide analyzer. NO_x and NO were measured using a "hot line", heated to about 120°C , to conduct the gas sample to the analyzer. Also, NO was measured using an unheated "cold line" to the analyzer. Hot line and cold line measurements were compared statistically as an indicator of measurement, and it was found that the hot line and cold line measurements agree very closely (see Reference 1, p. 32, 33).

Opacity was measured using Bacharach Smoke Spots, obtained with a Research Appliance Company Transmittance Particulate Monitor, modified to measure reflectance. The Monitor measured the reflected light from a spot on a paper tape that was soiled by passing flue gas through it for a fixed time period. Most of the reported data were taken with a standard hand pump device to pass the gas through the tape.

The analyzers for particulate, smoke spot, and sulfur oxides measurements were taken to the sample port. The weighing and titration were done in or near the EPA Mobile Air Pollution Reduction Laboratory trailer, and the NO_x analyzer was also located in the trailer. Further detail on the sampling and analysis procedures can be found in References 1-3.

7.4 SUMMARY

The available data were not collected for the purpose of developing alternate control options. Most of the data was developed with the emphasis on nitrogen oxide emission reduction by combustion modification and tended to neglect control measures for SO_x and particulate emissions. The bulk of the available data is for SO_x , NO_x , and particulate emissions from uncontrolled industrial boilers. There is a little data on electrostatic precipitators for control of particulate emissions from oil-fired industrial boilers, but there are no significant data on the emission reduction potential of POX, HDS, CAFB, and FGD, as applied to SO_x , NO_x , and particulate emissions from oil-fired industrial boilers.

Some useful trends for uncontrolled industrial boiler emissions may be found from the data, however. Sulfur oxide emissions and particulate emissions are highly dependent on the sulfur and ash contents of the oil, respectively. Nitrogen oxide emissions are dependent on fuel nitrogen content, as well as excess O_2 level and boiler size. In general, NO_x emissions decrease with decreasing excess O_2 and with increasing boiler size. The naturally low-sulfur, low-ash oils tended to meet at least the recommended control levels for moderate control in the oil cleaning category and quite often met even the intermediate or stringent control levels. The high-sulfur, high-ash oils, however, often failed to meet even moderate control levels, which suggests the need for oil cleaning or flue gas treatment.

The presently-available data, presented in this report, may thus prove valuable as a basis for comparison with emissions data from oil treatment technologies, which are not yet available.

REFERENCES

1. Cato, G. A., et al, "Field Testing: Application of Combustion Modifications to Control Pollutant Emissions From Industrial Boilers - Phase I," EPA-650/2-74-078a, October 1974.
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APPENDIX A

GLOSSARY OF TERMS

API gravity ($^{\circ}$ API): An arbitrary scale expressing the gravity or density of liquid petroleum products where the measuring scale is calculated in terms of degrees API by the following formula:

$$^{\circ} \text{API} = \frac{141.5}{\text{sp. gr. } 60^{\circ}\text{F}/60^{\circ}\text{F}} - 131.5$$

atmospheric residue: The heavy, less volatile liquid produced from distillation of petroleum at atmospheric pressure (frequently called resid or topped crude) whose boiling point is 650°F .

barrel: A common unit of liquid measurement in the petroleum industry; it equals 42 U. S. standard gallons.

catalyst: A substance which influences the rate of a chemical reaction but is not one of the original reactants or final products. A catalyst participates in intermediate chemical reaction steps in such a manner as to facilitate the over-all course of the reaction.

catalytic cracking: The process of selective decomposition of heavy distillate oils over a catalyst to produce gasoline, C_3/C_4 olefins, and isobutane.

catalytic reforming: The process of converting low octane naphthas into high octane naphthas by catalytically rearranging and dehydrogenating naphthenes and paraffins to form aromatic compounds.

coking: Thermal cracking of heavy, low-grade oils into lighter products and a solid residue of coke.

cracking: the reactions in which a hydrocarbon molecule is broken or fractured into two or more smaller fragments or the process of converting heavy oils into petroleum fractions of lower boiling range and corresponding lower molecular weight by thermally or catalytically fracturing the hydrocarbon molecule.

delayed coking: A thermal process applied to a residual oil stream which uses severe conditions ($1800\text{--}2000^{\circ}\text{F}$) to crack the feedstock to a coke gas, distillates, and coke.

demetallization: Removal of the organo-metal compounds by use of catalysts and heat in crude before processing so valuable catalysts are not poisoned by unwanted metals deposition.

denitrogenation: Removal of nitrogen compounds by catalysts to improve the quality of the petroleum product.

desalting: The removal of either sodium chloride and/or compounds that act like sodium chloride to prevent clogging, accumulation of undesirable compounds, decomposition and corrosion of refinery equipment.

GLOSSARY (continued)

- desulfurization:** The removal of undesirable sulfur and sulfur compounds from crude or residual oils so that end-use applications avoid violation of environmental regulations limiting sulfur levels in oil or emission standards.
- distillation:** Vaporization of a liquid and its subsequent condensation in a different chamber which allows separation of petroleum hydrocarbons by boiling point ranges.
- hydrocracking:** A process combining cracking or pyrolysis with hydrogenation over a catalyst bed to meet various product demands.
- hydrodesulfurization:** A catalytic process whereby a hydrocarbon feedstock and hydrogen are passed through a catalyst bed at elevated temperatures and pressures so that sulfur in the feedstock reacts with the hydrogen on the catalyst surface to produce hydrogen sulfide (H_2S) and a desulfurized hydrocarbon product.
- hydrogenation:** The chemical addition of hydrogen to a material. Hydrogen can be added to: (1) unsaturated compounds; or (2) in a destructive cracking case where the hydrocarbon chains have been broken.
- hydrotreating:** The use of hydrogen and a catalyst to purify, cleanse, and improve the quality of the feedstock with minimal reduction in molecular size of feed.
- petroleum:** A material occurring naturally in the earth, composed mainly of mixtures of chemical compounds of carbon and hydrogen with lesser amounts of sulfur, nitrogen, oxygen, and metals.
- pour point:** The lowest temperature at which a petroleum liquid will pour or flow when it is chilled under definite conditions.
- recycle:** That portion of a feedstock which has passed through a refining process and is recirculated through the process to achieve complete reaction or accumulate unwanted byproducts.
- residual oil:** Thick, heavy, semi-solid stream (produced as bottoms in distillation) which is high boiling and contains undesirable levels of organo-metallic and organo-sulfur compounds. Commonly called resid.
- residue:** Heavy oil or bottoms left in the still after gasoline and other relatively low-boiling hydrocarbons have been distilled off.
- thermal cracking:** The use of heat to achieve cracking or fracturing of the hydrocarbon molecule.
- vacuum gas oil:** The heavy fuel oil produced when atmospheric residue is distilled at a pressure of 50 mm Hg. Boiling point range is 343-566°C (650-1050°F).
- vacuum residue:** The heavy, thick bottoms (pitch) produced by distillation of atmospheric residue under 50 mm Hg pressure whose boiling point exceeds 980°F.

GLOSSARY (continued)

visbreaking: A thermal cracking process which lowers the viscosity of residual oil to lessen the amount of blending stock required to upgrade the residual to fuel oil specifications.

APPENDIX B

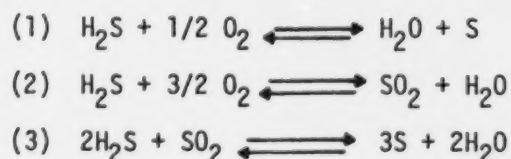
SULFUR RECOVERY SYSTEMS FOR OFF-GAS TREATMENT

Hydrogen sulfide gases are released during the regeneration of amine or other scrubbing solutions which are used to desulfurize refinery process gases such as those produced by hydrodesulfurization. In addition, some H_2S is removed from process water by sour water strippers. Most refineries include facilities for steam stripping H_2S from sour water streams as part of the waste water system. Where sulfur recovery is practiced, the off-gases from the stripper are normally routed to the sulfur recovery plant.

In the CAFB process, SO_2 is produced in the regeneration cycle; and, different techniques are used to collect it. These are discussed below after the methods for H_2S recovery.

The Claus Process

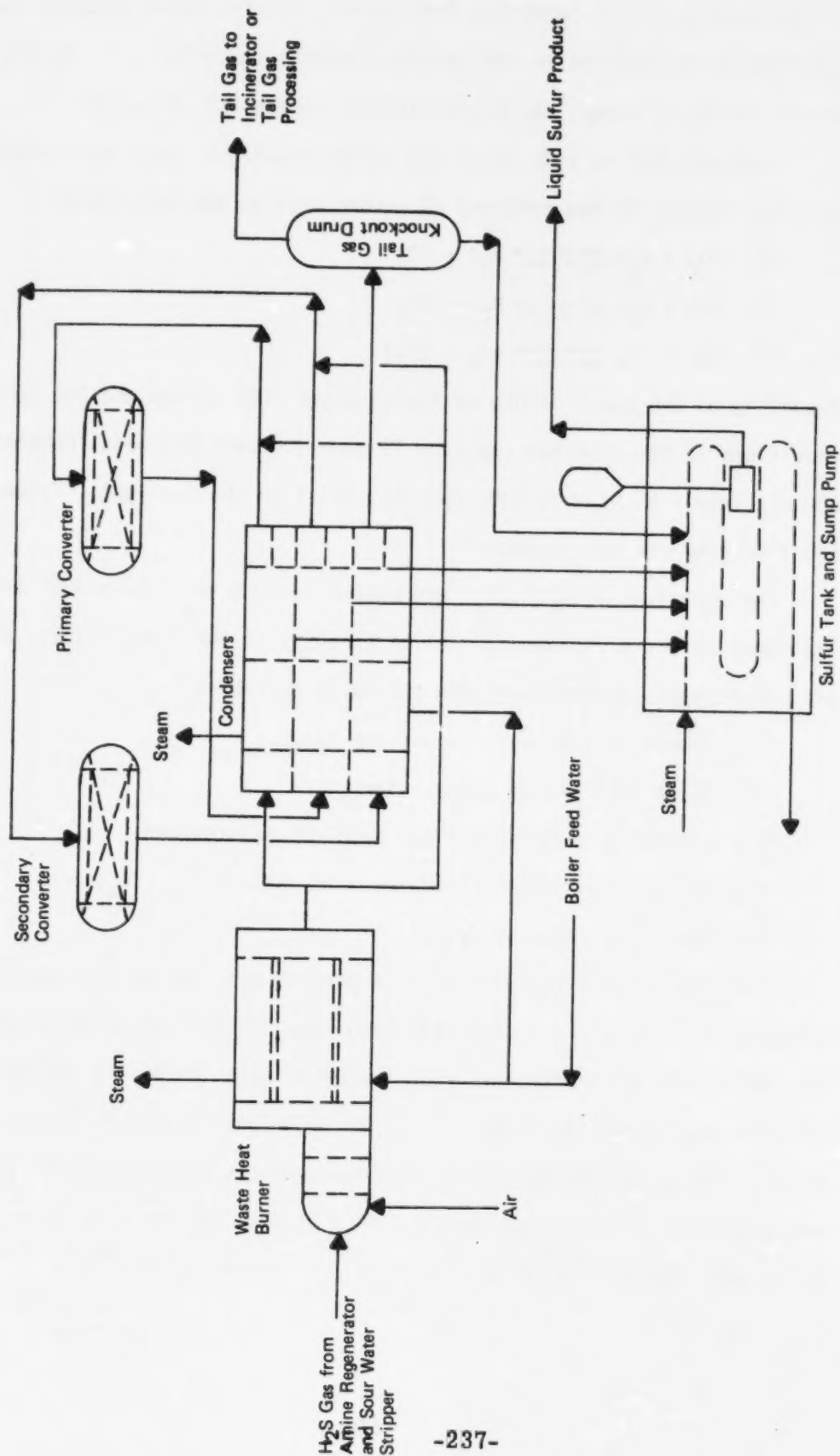
The Claus process has been used almost exclusively in petroleum refineries to recover sulfur. The basic exothermic reactions for the Claus process are:



A typical two-stage Claus plant is shown in Figure B-1. Hydrogen sulfide gas enters the burner with sufficient air to convert all H_2S to sulfur. As much as 50 to 60 percent conversion of the hydrogen sulfide to sulfur takes place in the initial reaction chamber by Reaction (1). Reaction (2) also takes place, forming SO_2 . After cooling, condensing, and removing sulfur, the gases are reheated by mixing with a portion of the gases bypassed around the sulfur condenser and introduced into the first catalytic reactor, where the Claus reaction (Reaction (3)) occurs. From the first catalytic reactor, the effluent

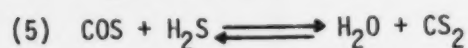
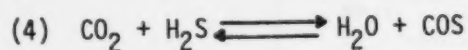
Figure B-1

TYPICAL PACKAGED CLAUS PLANT (2 STAGE)



gas is cooled, sulfur condensed and removed, and the gases reheated again. The process is repeated in the second catalytic converter. If needed, additional catalytic stages may be utilized to remove H_2S as sulfur.

Some carbonyl sulfide (COS) and carbon disulfide (CS_2) are formed in the reaction furnace in the presence of carbon dioxide and hydrocarbons:



Depending on the exact nature of the sour-gas feed stream and the operating conditions in the upstream reaction furnace and catalyst beds, combined COS and CS_2 levels as high as 5000 ppmv may exist in the tail-gas. Values of 600-1500 ppmv are more common.

The emissions of H_2S , SO_2 , and sulfur vapor from Claus plants are directly dependent on the efficiency of sulfur recovery in the Claus plant. Claus plant efficiencies are dependent on the following variables:

- (1) number of catalytic conversion stages;
- (2) inlet feed stream composition;
- (3) operating temperatures and catalyst maintenance;
- (4) maintaining proper stoichiometric ratio of $\text{H}_2\text{S}/\text{SO}_2$; and
- (5) operating capacity factor

For Claus plants fed with 90 mole percent H_2S , the sulfur recovery is approximately 85% for one catalytic stage and 95% for two or three stages. The percentage sulfur recovery also increases with increasing concentration of the acid gas fed to the Claus unit. For plants having two or three catalytic stages, the sulfur recoveries for various acid gas concentrations are approximately 90% for a 15 mole percent H_2S feed stream, 93% for a 50 mole percent H_2S stream, and 95% for 90 mole percent H_2S concentration.⁽²⁾

Contaminants in the feed gas reduce Claus sulfur recovery efficiency. Hydrocarbons in Claus feedstocks require extra air for combustion. The added water and inert gas associated with burning hydrocarbons increases the size of the sulfur plant equipment and lowers sulfur recovery, since the sulfur gas concentrations are decreased.⁽³⁾ High molecular weight hydrocarbons in the feed also reduce Claus efficiencies because of carbon soot deposition on the catalyst. Since the reactions in a Claus plant are exothermic, sulfur recovery is enhanced by removing heat; hence, operation at as low a temperature as practical in the reactors without condensing sulfur on the catalyst is necessary.

Although sulfur recovery efficiencies of 94-96% are possible in standard multiple-stage Claus units, these are insufficient to meet most air pollution control regulations. The tail-gas, containing 4-6% of the input sulfur value, is usually incinerated by thermal or catalytic means. Desulfurization of Claus tail-gas has received increasing attention for two reasons: (1) the increase in desulfurization activity has resulted in an increase in sulfur dioxide emissions from the Claus system; and (2) the off-gas is particulate free and high in hydrogen sulfide concentration (up to 1500 ppm) and is thus easier to treat than ordinary flue gas. The treatment of Claus off-gas can follow one of many schemes whose basic treatment methodologies are shown in Figure B-2. With application of the Claus off-gas cleanup units, the overall sulfur removal efficiency (Claus included) generally exceeds 99.5% for the treatment systems whose descriptions follow.

Beavon Process (Figure B-3)⁽⁴⁾

The Beavon Process involves hydrogenation of the other sulfurous gases (carbon disulfide, carbonyl sulfide) in the Claus tail-gas to hydrogen sulfide over a cobalt-molybdate catalyst at moderate temperature and pressure. This catalyst effectively promotes the reaction between water vapor and carbon

Figure B-2

EMISSION CONTROL SYSTEMS FOR REFINERY CLAUUS PLANTS

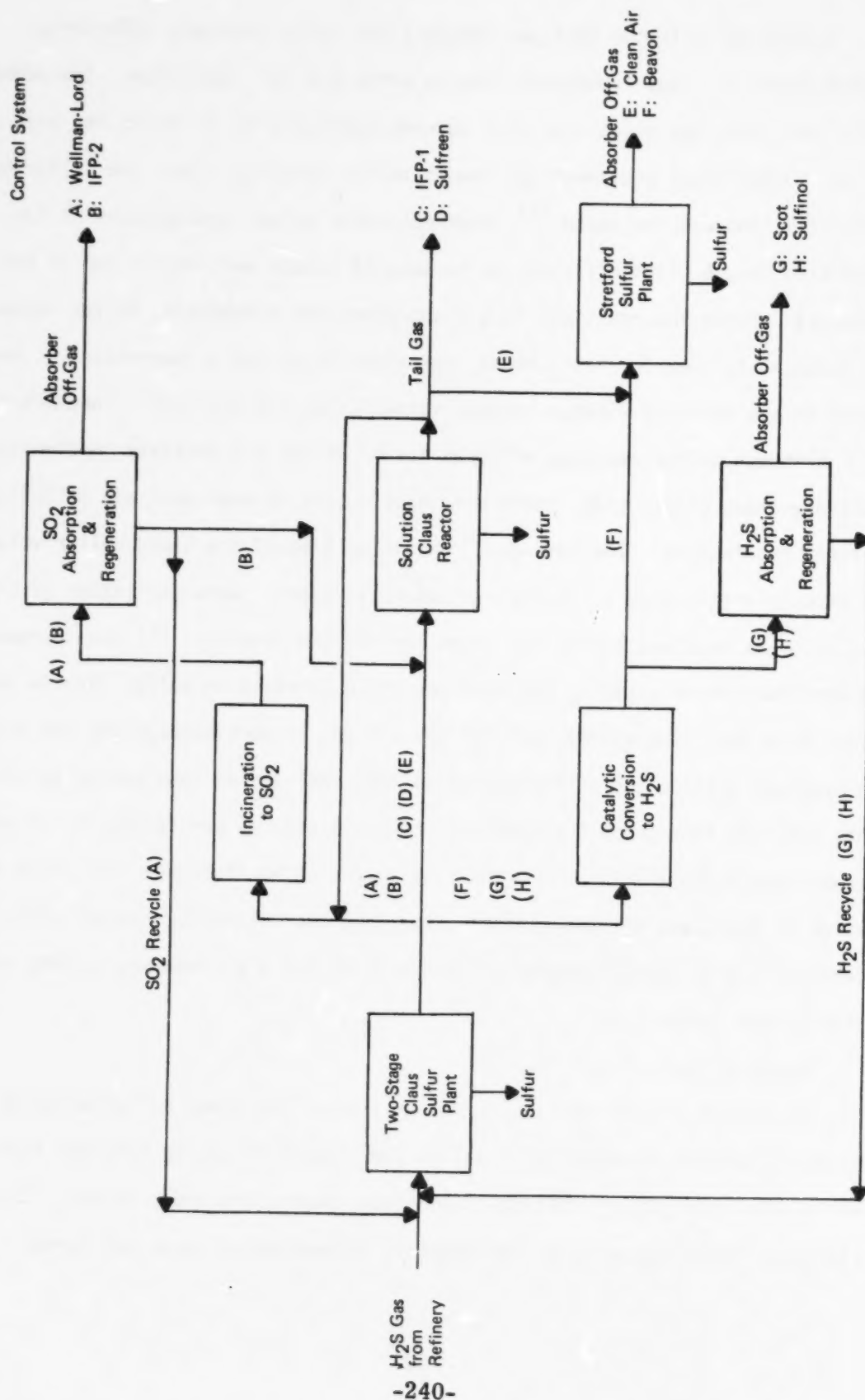
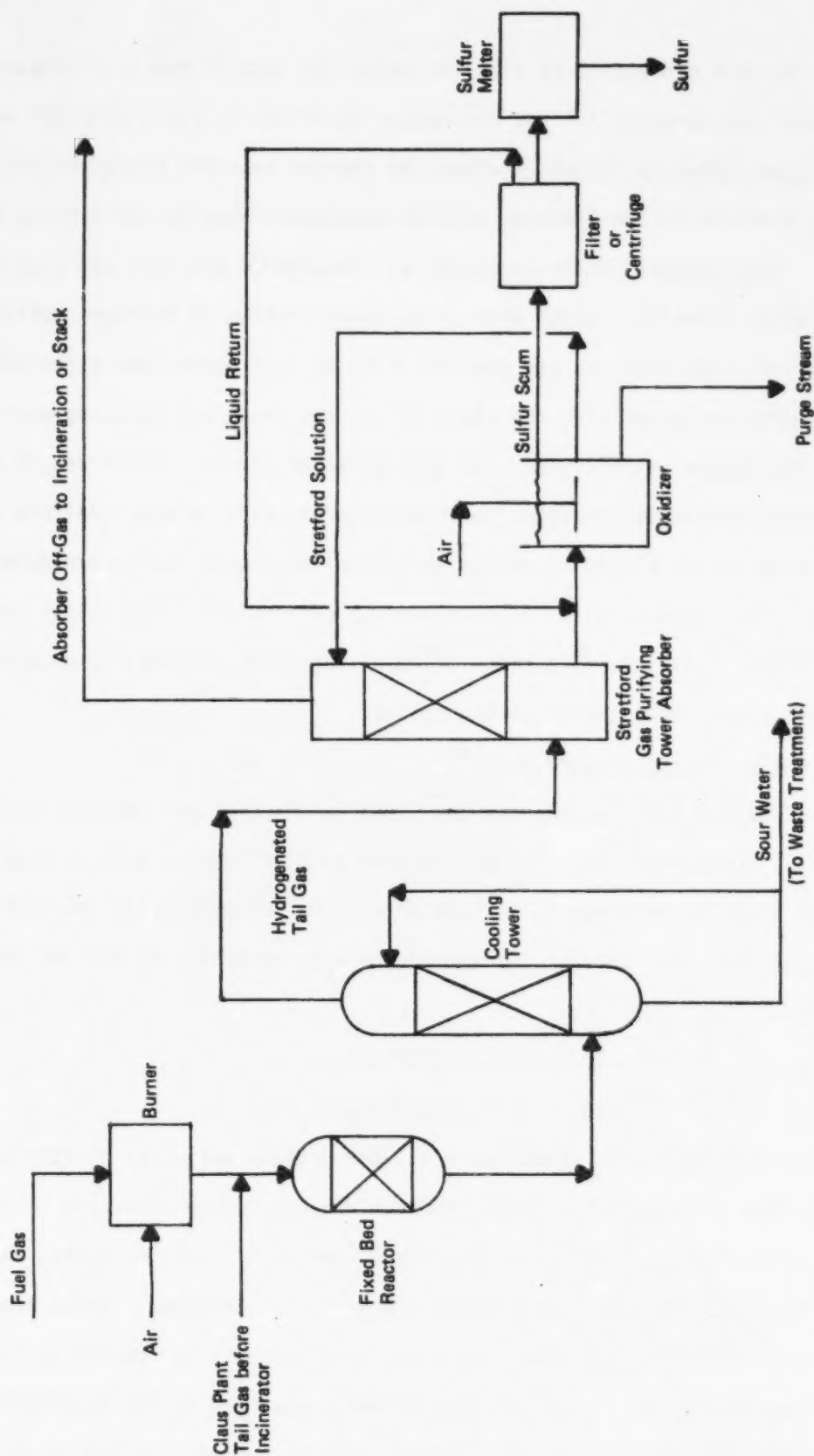


Figure B-3
FLOW DIAGRAM FOR THE BEAVON SULFUR REMOVAL PROCESS



monoxide to form hydrogen. It also increases the rate of reaction between water vapor and carbonyl sulfide and carbon disulfide to yield hydrogen sulfide. Excess water is condensed after the reactor to avoid corrosion and plugging problems in the hydrogen sulfide conversion step by the Stretford Process. That process can be conducted at atmospheric pressure and produces a high-purity elemental sulfur with a low concentration of hydrogen sulfide effluent. Air and fuel gas are reacted in an in-line burner where the combustion products are mixed with the Claus off-gas to produce a reducing environment in the Beavon reactor where the hydrogenation occurs. The hydrogen sulfide product stream is converted to sodium hydrosulfide in the Stretford Process. Oxidation to elemental sulfur is accomplished over sodium vanadate in solution. The product sulfur is recovered by conventional fine-solids concentration steps: washing, filtration or centrifugation, followed by decantation after melting and coagulation of the sulfur.

Cleanair Process (Figure B-4)⁽⁵⁾

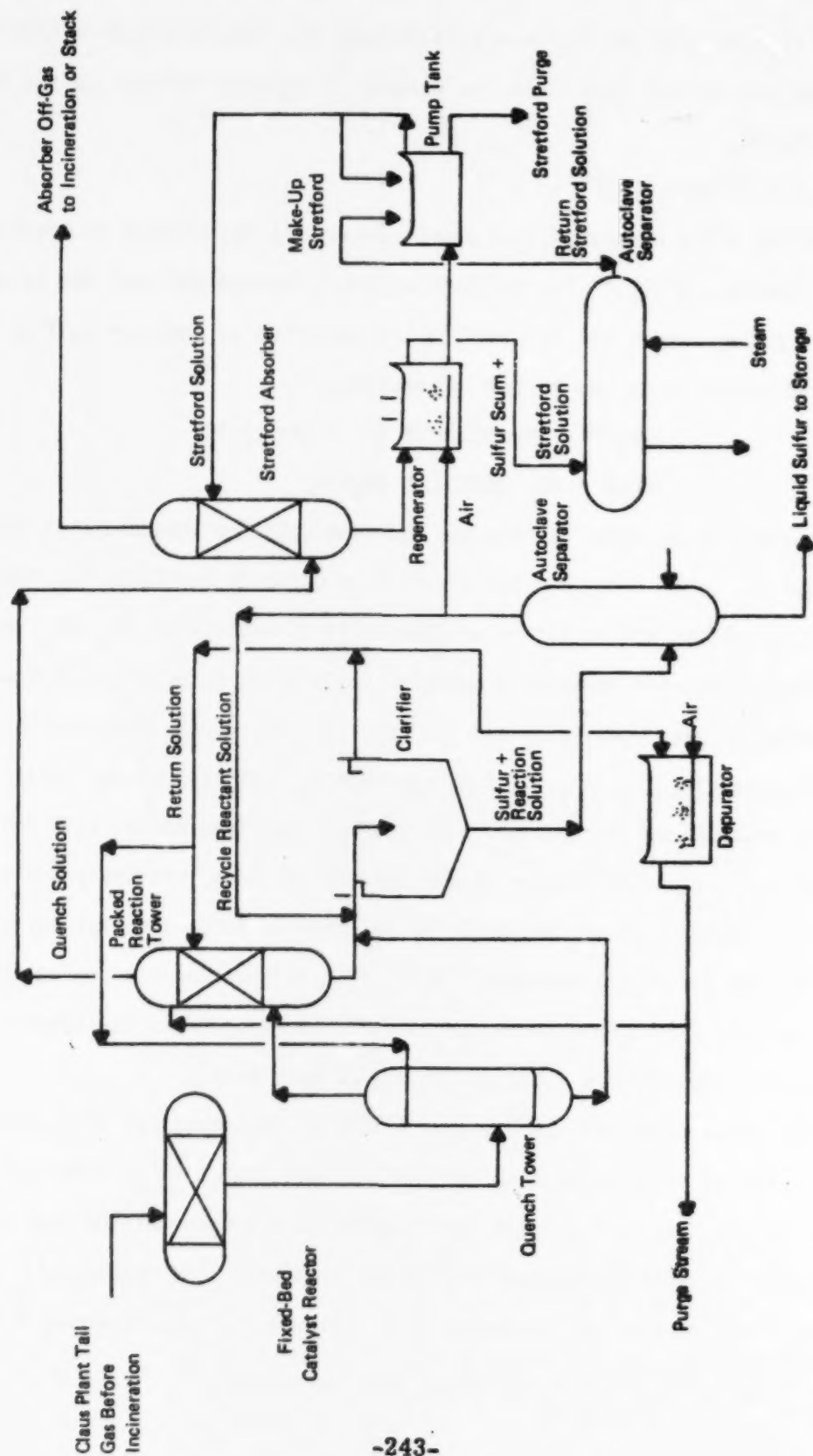
The Cleanair Process includes the Stretford Process and two confidential processes. An optional part of the Cleanair unit includes a modification of the Claus plant first stage to include a reducing and hydrolysis catalyst. This causes the conversion of COS and CS₂ to H₂S, according to the following reaction:



Claus tail-gas, with essentially all the gaseous sulfur as sulfur vapor, H₂S, and SO₂, is quenched to reduce temperature and remove water and entrained sulfur. The cooled gas is fed into a reactor where H₂S and SO₂ react, lowering SO₂ to less than 250 ppmv. Both water and sulfur are removed. Next, the tail-gas is sent to a Stretford unit, where the remaining H₂S is removed and oxidized to elemental sulfur. Residual SO₂, although absorbed by the Stretford solution, decomposes the solution to increase chemical consumption and liquid purge

Figure B-4

FLOW DIAGRAM FOR THE CLEANAIR CLAUS TAIL-GAS TREATMENT PROCESS



rate. Residual COS and CS₂ will pass through the Stretford unit unaffected. Purified gas is then sent to an incinerator to oxidize residual sulfur to SO₂ and CO to CO₂.

IFP-2 (Figure B-5)⁽⁶⁾

In the IFP-2 Process, Claus plant tail-gas is incinerated to convert all sulfur species to SO₂.^{*} The incinerated gas is cooled and then fed to an ammonia scrubber, where SO₂ is absorbed and converted to ammonium sulfite and ammonium bisulfite by the following reactions:



Gas leaving the absorber is reheated and vented to the atmosphere at less than 250 ppmv SO₂ concentration. The SO₂-rich solution is fed to an SO₂ regenerator where the sulfite and bisulfite are thermally decomposed to SO₂, NH₃, and H₂O. A saturated solution containing ammonium sulfate and thiosulfate is drawn from the bottom of the regenerator and fed to a sulfate reducer where it is thermally reduced, creating SO₂, NH₃, S, H₂O, and NH₄HSO₄. Gases from the sulfate reducer and SO₂ regenerator are combined with the H₂S-rich feed stream from the Claus unit and fed to a catalytic reactor where they are contacted with polyethylene glycol solvent. The H₂S and SO₂ react in the solution to form elemental sulfur, which is withdrawn in the molten state. Gases from the reactor are cooled to condense water and NH₃ and NH₄OH. The NH₄OH solution is returned to the ammonia scrubber.

Shell Claus Off-Gas Treating Process (Figure B-6)⁽⁷⁾⁽⁸⁾

The Shell Claus Off-Gas Treating (SCOT) Process consists of a reduction section and an amine absorption section. In the reduction section, all sulfur values in the Claus off-gas are hydrogenated to hydrogen sulfide over a cobalt/molybdenum catalyst (supported on alumina) at 300°C. The reactor effluent is cooled, and the water is condensed. The effluent, containing about 3% H₂S and

^{*} IFP-2 has replaced IFP-1, which was less efficient and is not discussed here.

Figure B-5

FLOW DIAGRAM FOR IFP-2 CLAUS TAIL-GAS CLEAN-UP PROCESS

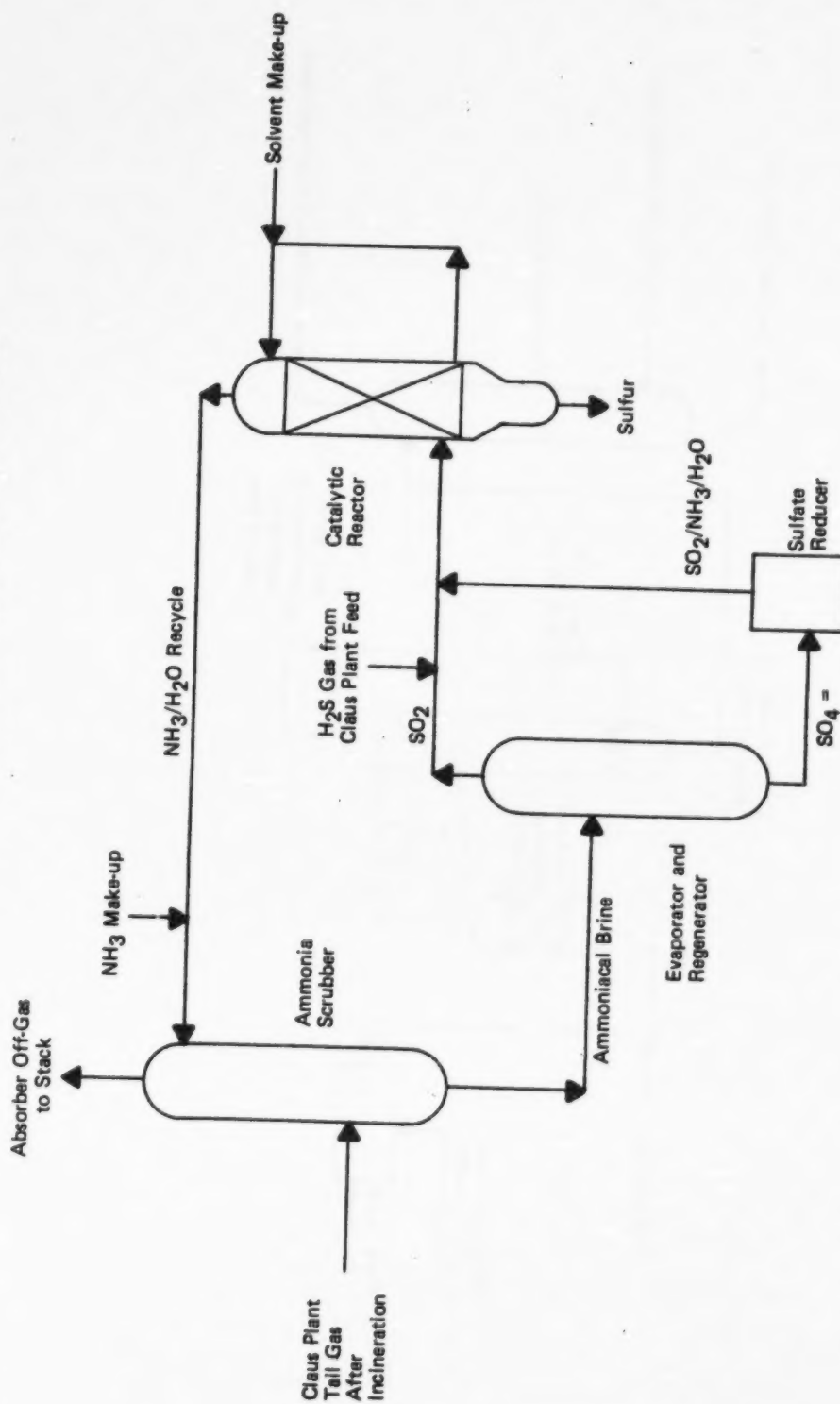
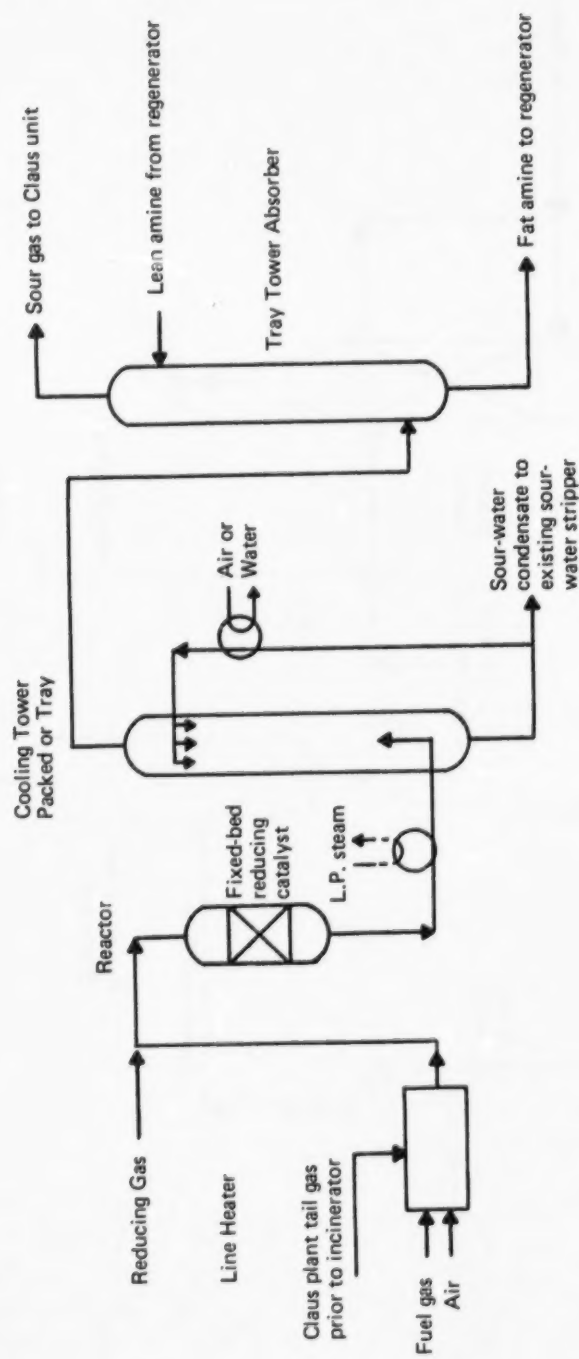


Figure B-6
FLOW DIAGRAM FOR THE SHELL CLAUSS OFF-GAS TREATING PROCESS

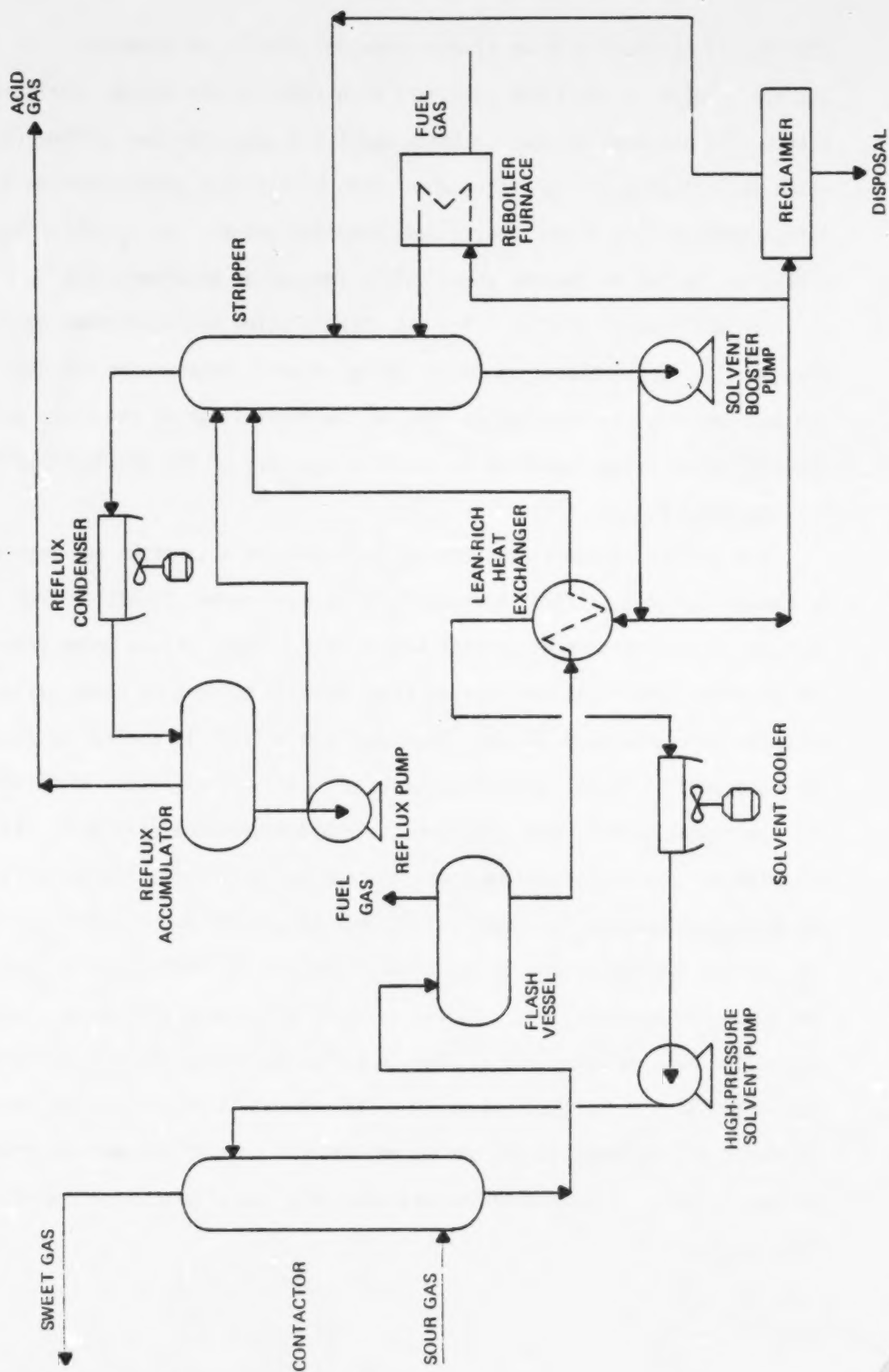


20% CO_2 , is scrubbed with an alkanolamine solution in an absorber. COS and CS_2 are reduced in reactions identical with those in the Beavon catalytic reactor. The absorber off-gas contains about 300 ppmv hydrogen sulfide (H_2S), which is incinerated. Selective absorption of H_2S over carbon dioxide is obtained because of a difference in mass transfer rates. The H_2S absorption is diffusion-limited in the gas phase and is removed by treatment with di-isopropanolamine solution. The H_2S -rich solution is regenerated by stripping H_2S in a conventional steam stripping column. Regenerator off-gas, mainly H_2S and some CO_2 , is recycled as feed to the first stage of the Claus unit. The SCOT Process can result in up to 99.8% recovery of all the input sulfur.

Sulfinol Process (Figure B-7)⁽⁹⁾

The Sulfinol Process uses conventional solvent absorption and regeneration to remove carbonyl sulfide, hydrogen sulfide, and carbon disulfide from Claus tail-gas by countercurrent contact with a lean solvent stream under pressure. The absorbed impurities are removed from the rich solvent by steam stripping in a heated regenerator column. The hot, lean solvent is cooled for reuse in the absorber. Sulfinol solvent consists of a mixture of water, an alkanolamine (di-isopropanolamine), and sulfolane (tetrahydrothiophene dioxide). The alkanolamine absorbs acid gases by chemical combination. The sulfolane allows high solution loadings and low regeneration heat requirements. The Sulfinol Process can achieve H_2S reductions to less than 1 ppm and CO_2 reductions to less than 100 ppm. The combination of the two solvents gives good absorptive properties for sulfur gaseous compounds at low- to medium-partial pressures and very high absorption at high partial pressures. The process is nonfoaming and noncorrosive to steel, and equipment costs can be minimized. Loss of solvent components is minimal, since sulfolane does not degrade; and, the alkanolamine regeneration step minimizes those losses.

Figure B-7
SULFINOL PROCESS (9)



Sulfreen Process (Figure B-8)⁽¹⁰⁾⁽¹¹⁾

The Sulfreen Process reduces the sulfur content in Claus plant tail gas by further promoting the Claus reaction on a catalytic surface in a gas/solid batch reactor. Claus tail gas is first scrubbed with liquid to wash out entrained sulfur liquid and sulfur vapor. The tail gas is then introduced to a battery of reactors where the Claus reactions are carried out at lower temperatures (260-300°F) than those utilized in the sulfur plant. Lower temperatures push the Claus reaction toward completion due to favorable equilibrium conditions. The catalyst is usually activated carbon, though alumina can be used. A regeneration gas, usually nitrogen, periodically desorbs the sulfur-laden catalyst beds. Nitrogen is treated and cycles through the catalyst bed at approximately 570°F until all water and CO₂ are driven off. For the desorption of sulfur, the temperature is raised to 750°F, where sulfur vaporizes, is swept away with the nitrogen, and precipitates in a condenser. The carrier gas is further scrubbed in a sulfur wash before returning to the regeneration cycle.

The process reduces entrained sulfur, since the catalyst acts as an absorbent for liquid sulfur. COS and CS₂ are not affected by the Sulfreen Process. A Sulfreen unit may consist of as little as three reactors; two in absorption, and one in desorption service. The gases from the desorption service are incinerated before discharge to the atmosphere.

Wellman-Lord SO₂ Recovery Process (Figure B-9)⁽¹²⁾

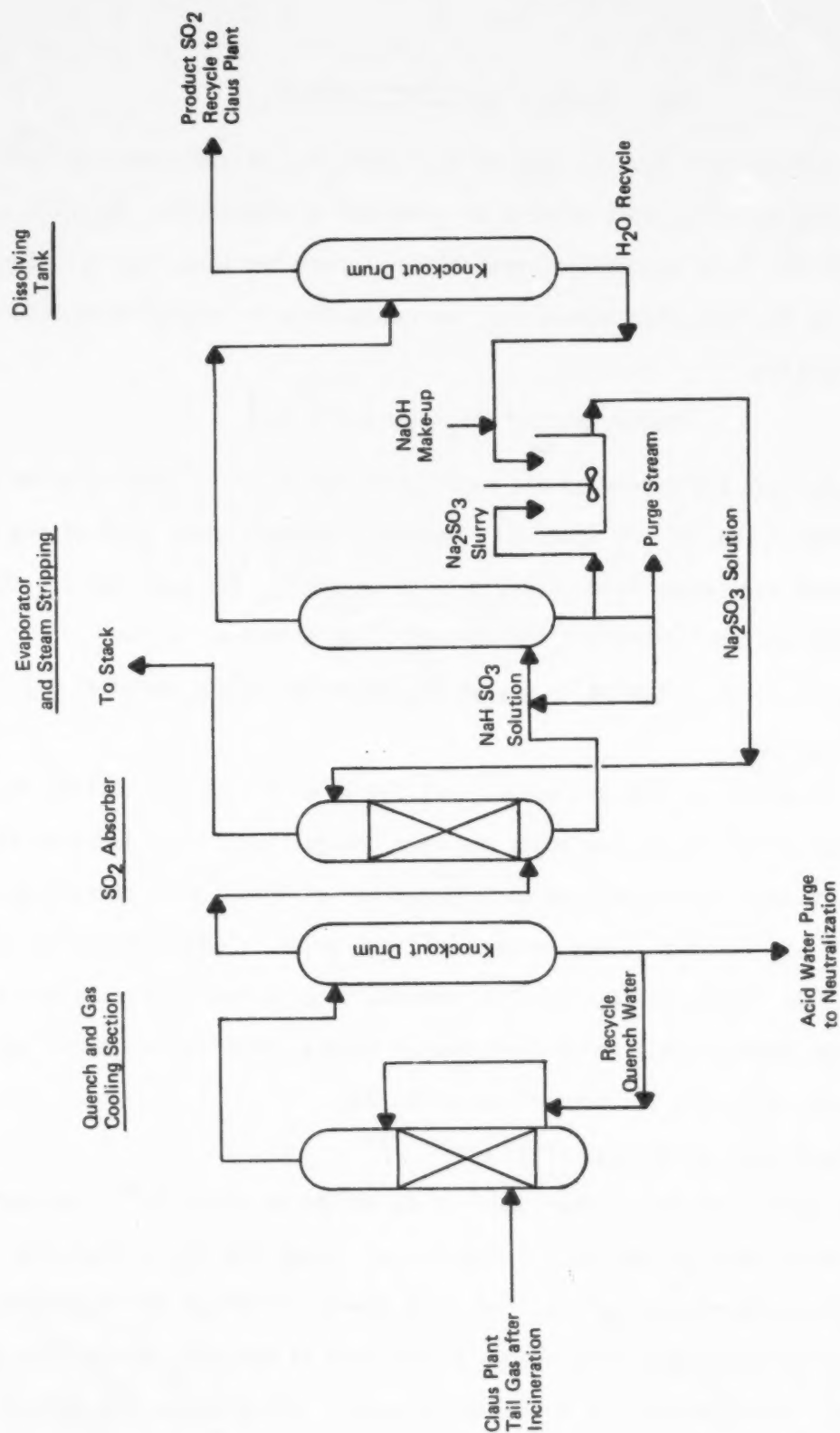
The Wellman-Lord Process uses a wet regenerative system to reduce the stack gas sulfur concentration to less than 250 ppmv. Sulfur constituents in Claus plant tail-gas are oxidized to SO₂ in an incinerator, then cooled and quenched to reduce the gas temperature and remove excess water. The SO₂-rich gas is then contacted countercurrently with a sodium sulfite (Na₂SO₃) and sodium bisulfite (NaHSO₃) solution which absorbs SO₂ to form additional bisulfite. The principal reaction between SO₂ and the absorbent solution is:

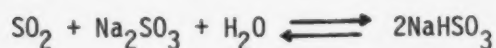
FLOW DIAGRAM FOR THE SULFREEN PROCESS



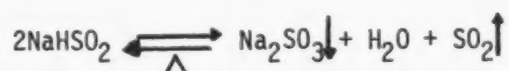
Figure B-9

FLOW DIAGRAM FOR THE WELLMAN-LORD SO_2 RECOVERY PROCESS





The absorber off-gas is reheated and vented to the atmosphere at less than 250 ppmv SO_2 and negligible amounts of other sulfur compounds. SO_2 -rich solution is boiled in an evaporator-crystallizer, where the bisulfite solution decomposes to SO_2 and water vapor; and, sodium sulfite is precipitated according to the reaction:



Sulfite crystals are separated and redissolved for reuse as lean solution to the scrubber. The wet SO_2 flows to a partial condenser where most of the water is condensed and reused to dissolve sulfite crystals. The enriched SO_2 stream is recycled to the Claus plant for conversion to elemental sulfur.

Special Cases - Chemically Active Fluidized Bed (CAFB) Residual Oil Gasification Systems

In regenerative CAFB processes, sulfided lime is oxidized to lime in the regenerator prior to its recirculation into the gasifier. SO_2 is given off as a result of this oxidation, and the regenerator off-gases will contain as much as 6 to 8 percent SO_2 . Since release of these gases is environmentally unacceptable, the sulfur content must be removed. The following discussion covers the Allied Chemical (AC) and Foster Wheeler Energy Corporation's RESOX systems for conversion of the SO_2 into elemental sulfur.

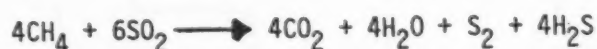
Allied Chemical Process (Figure B-10)⁽¹³⁾

The gases from the regenerator must be cooled to about 300°F, and particulate material must be removed. A blower then forces the SO_2 through the reduction system with natural gas as a reducing agent. Although the SO_2 -natural gas reduction is exothermic, some oxygen in the form of air must be admitted at the blower inlet to maintain a thermal balance. This mixture then passes through the feed gas preheater where its temperature is raised above the dew

ALLIED CHEMICAL SO₂ REDUCTION PROCESS



point of the sulfur formed in the primary reactor system. The gas then enters the catalytic system where hydrogen sulfide and sulfur are produced. The $\text{H}_2\text{S}/\text{SO}_2$ ratio in the gas stream leaving the system is essentially that required for the subsequent Claus reaction. The reactions taking place in the primary reaction system are:



Because of the exothermic reaction, a portion of the available heat is used to preheat the incoming gases in the feed gas heater. The elemental sulfur formed is condensed in a horizontal shell-and-tube condenser where over 40% of the total sulfur is recovered. The process gas next enters a two-stage Claus reactor where the following exothermic reaction occurs:



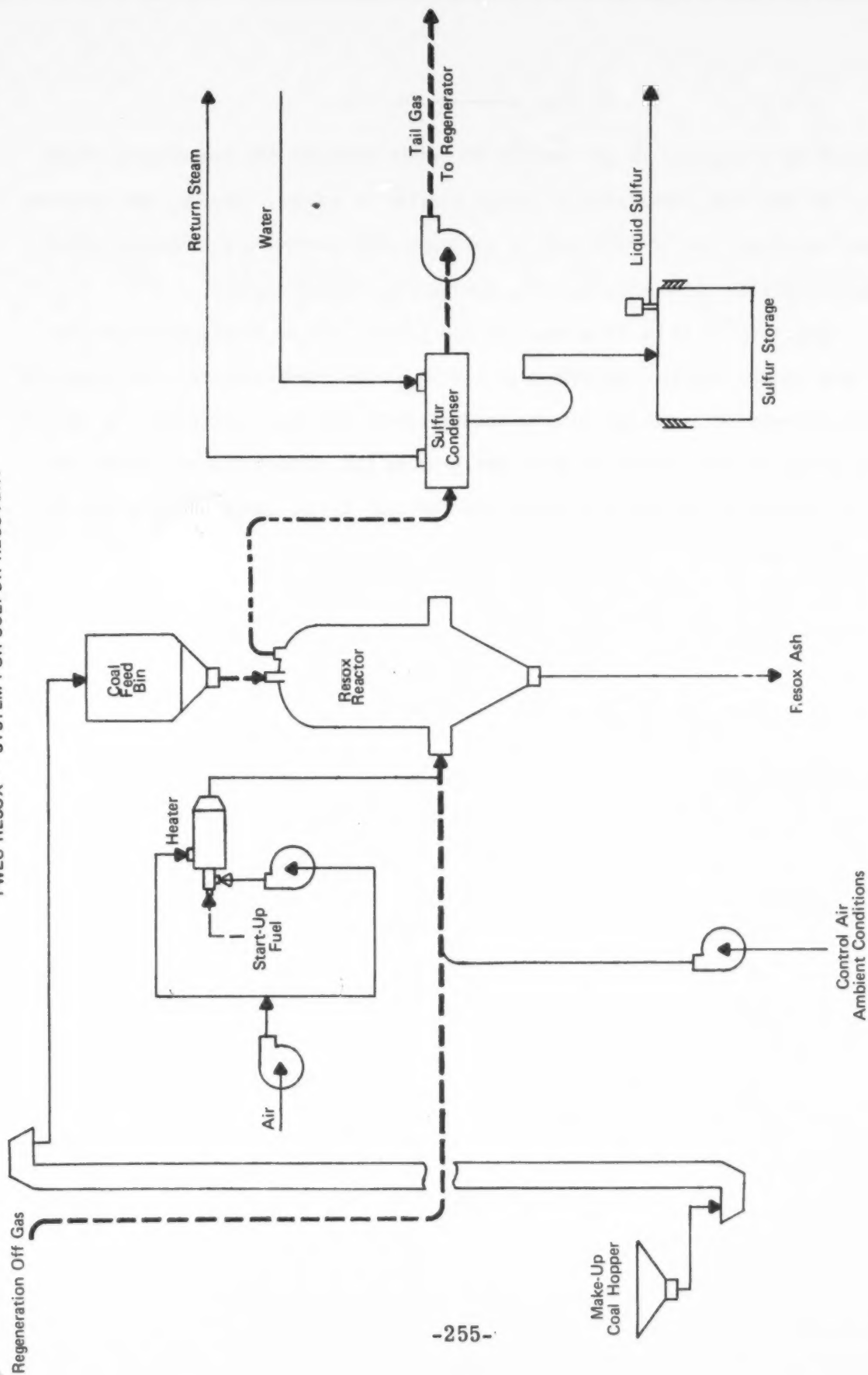
After the first stage of Claus conversion, the gas is cooled; and, additional sulfur is condensed by passage through a vertical condenser. Further conversion of H_2S and SO_2 to sulfur takes place in the second stage Claus reactor. This sulfur is condensed in a third condenser. Residual sulfur gases are returned to the CAFB gasifier where they react and are retained by the active lime bed.

Foster-Wheeler Energy Corporation - RESOX (Figure B-11)⁽¹³⁾

Gases from the regenerator are reduced to about 1200°F , the required reactor inlet temperature, by the injection of steam or water. This steam injection also produces the proper $\text{H}_2\text{O}/\text{SO}_2$ ratio. Control air and the process is fed to the RESOX reactor. The air furnishes the limited amount of oxygen needed for maintaining and controlling reactor temperature $200\text{--}300^\circ\text{F}$ above the inlet conditions. The overall reaction in the RESOX reactor is:

Figure B-11

FWEC RESOX™ SYSTEM FOR SULFUR RECOVERY





Although this reaction is exothermic, it cannot maintain the temperature necessary for the high conversion of sulfur dioxide to sulfur. Carbon, the reducing agent required, can be furnished by any coal with performance characteristics compatible with the countercurrent, moving-bed, reactor system.

Reduction of 75 to 90 percent of the sulfur dioxide to elemental sulfur is made in the reactor, depending on the SO_2 inlet concentration. The elemental sulfur formed is condensed in a horizontal shell-and-tube condenser. An ID fan downstream of this condenser moves the process gas through the system and returns off-gas to the gasifier where the residual sulfur gases are absorbed by the fluidized bed.

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